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40th Annual Actinide Separations Conference

J. A. McNeese

May 12, 2016

40th Annual Actinide Separations Conference
San Diego, CA, United States
May 24, 2016 through May 26, 2016

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*40th Annual
Actinide Separations Conference*



Hilton San Diego/Del Mar

San Diego, CA

May 24-26, 2016



Welcome to the 40th Actinide Separations Conference

Welcome to the 40th Actinide Separations Conference, hosted this year by Lawrence Livermore National Laboratory. With your active participation and papers on many interesting topics, we look forward to a valuable and informative technical interchange. There is no other conference that provides a similar venue for applied science work directed towards DOE actinide missions. The Actinide Separations Conference provides a forum where physicists, chemists, radiochemists, and a variety of engineering disciplines (nuclear, chemical, mechanical) can interact in scientific and practical way. It's an opportunity for peer review of developing work and professional interactions between DOE professionals and university professors and students.

Thank you for coming and we hope you enjoy the conference.

Conference Chair

James McNeese

Conference Coordinator

Lisa Palmer

Conference Management

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Auspices

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Authorship

Each participant is responsible for ensuring their contribution is reviewed for release by their organization to include intellectual property and export control.

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Actinide Separations Conference Advisory Board Members

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Kenneth L. Nash

Washington State University

Mikael Nilsson

University of California, Irvine

Bradley E. Skidmore

Los Alamos National Laboratory

Conference Schedule

Hilton Garden Inn

Grande Ball Room

Monday – May 23, 2016

Registration/Check-In – Abstract books available for pickup 5:00 -7:00 PM

Tuesday – May 24, 2016

Check-In 7:30 AM

Plenary Session 8:00 AM

Lunch (on own) 12:00 PM

Session 1: Aqueous Processing and Oxide Characterization 1:30 PM

Poster Session 6:00 – 8:00 PM

Wednesday – May 25, 2016

Session 2: Sigma Team for Minor Actinide Separations 8:00 AM

Afternoon Open for Other Discussions 12:00 Noon

Advisory Board Meeting (closed session: Location Torrey Pines Board Room @ Homewood Suites) 12:00 Noon

Sigma Team for Minor Actinide Separations Research Meeting 1:30 PM

Thursday – May 26, 2016

Session 3: Sigma Team for Minor Actinide Separations 8:00 AM

Lunch (on own) 12:00 PM

Session 4: Separation Processing 1:30 PM

Conference Banquet and Seaborg Award Presentation 6:30 – 9:00 PM

Glenn T. Seaborg Actinide Separations Award

- 1984 Glenn T. Seaborg, *University of California-Berkeley*
1985 Don E. Ferguson, *Oak Ridge National Laboratory*
1986 Larned B. Asprey, *Los Alamos National Laboratory*
1987 Wallace W. Schulz, *Westinghouse Hanford Company*
1988 Lawrence J. Mullins, *Los Alamos National Laboratory*
1989 Gregory R. Choppin, *Florida State University*
1990 Donald A. Orth, *Westinghouse Savannah River Company*
1991 David O. Campbell, *Oak Ridge National Laboratory*
1992 E. Philip Horwitz, *Argonne National Laboratory*
1993 Earl J. Wheelwright, *Pacific Northwest Laboratory*
1994 Leslie Burris, *Argonne National Laboratory*
1995 Robert R. Penneman, *Los Alamos National Laboratory*
1996 David G. Karraker, *Westinghouse Savannah River Company*
1997 Major C. Thompson, *Westinghouse Savannah River Company*
1998 Walter D. Bond, *Oak Ridge National Laboratory*
1999 Jack L. Ryan, *Pacific Northwest National Laboratory*
2000 John L. Swanson, *Pacific Northwest National Laboratory*
2001 George F. Vandegrift, *Argonne National Laboratory*
2002 Leonard W. Gray, *Lawrence Livermore National Laboratory*
2003 Kenneth L. Nash, *Argonne National Laboratory*
2004 Emory D. Collins, *Oak Ridge National Laboratory*
2005 Terry A. Todd, *Idaho National Laboratory*
2006 Renato Chiarizia, *Argonne National Laboratory*
2007 Leland L. Burger, *Pacific Northwest National Laboratory*
2008 Gordon D. Jarvinen, *Los Alamos National Laboratory*
2009 Raymond G. Wymer, *Oak Ridge National Laboratory*
2011 Darleane C. Hoffman, *University of California-Berkeley*
2012 Jimmy T. Bell, *Oak Ridge National Laboratory*
2013 Lane A. Bray, *Pacific Northwest National Laboratory*
2014 David T. Hobbs, *Savannah River National Laboratory*
2015 Gregg J. Lumetta, *Pacific Northwest National Laboratory*

2016 Glenn T. Seaborg Actinide Separations Award Winner

Dr. Guillermo (Bill) Daniel Del Cul

Guillermo (Bill) Del Cul completed his B.S. degree in Chemistry in March of 1976 and his M.S. degree in Physical Chemistry at the La Plata National University in Argentina in December of 1977. During undergraduate and graduate school, he was a teaching and research assistant in general and inorganic chemistry. His major topics of research included fluorine-based chemistry and the extraction and purification of Zr, Hf and Th from natural deposits of sand in Argentina.

Dr. Del Cul completed his Ph.D. in Inorganic Chemistry at the University of Tennessee in December of 1990 working on chemistry and spectroscopy of transuranium elements at the Oak Ridge National Laboratory.

Bill became a citizen of the United States of America in 1999.

His professional career started at the National Institute of Industrial Technology (Argentina) in 1978 working on gas chromatography separations for industrial applications. Then in 1981, he moved to an oil company as section head of thermodynamic studies, to work on collecting deep samples from an oil field at high pressures and temperatures using a remote tool, and then simulating in the laboratory, the evolution of the production conditions over time, and the chemical composition of oil and gas recoverable until the depletion of the reservoir.

In 1981, Bill joined the Argentina National Atomic Energy Commission and started working as a member of the enriched uranium laboratory group. One of the main activities included the recovery of highly enriched uranium from scrap and residues, using solvent extraction for purification, followed by selective precipitation, hydro-fluorination, and bomb reduction to metal. In 1985, Bill obtained a nuclear license as shift supervisor of the enriched uranium laboratory in 1985. In parallel, the group was taking part in the design and construction of a pilot-scale reprocessing plant, based on the PUREX process and Bill was working on the plutonium development section. The plant was never completed and work stopped at the end of 1985.

In March 1986, Bill moved to the United States and started working at Oak Ridge National Laboratory in the Chemical Technology Division. During Bill's initial years, he worked as a member of a team developing grout-based waste forms for a variety of nuclear wastes from the Hanford, ORNL and Savannah River sites, and in parallel, Bill was working on his doctoral dissertation related to the chemistry and spectroscopy of transuranic elements.

In 1990, Bill transferred to the Oak Ridge Gaseous Diffusion Plant (K-25) and joined the technical division supporting the operations of the gaseous diffusion plants at Paducah and Portsmouth, and the decontamination activities at the K-25 Site. In October 1993, Bill returned to ORNL to work in high temperature molten salts for different applications such as molten salt reactors, molten salt oxidation, gallium removal, accelerator-driven systems, U.S. Navy applications, remediation of the Oak Ridge molten salt reactor, and fluoride volatility processes. Bill was a co-inventor of "TRU-FLUOR", an innovative fluoride volatility process for used nuclear fuel.

In 1999, Bill became a key participant in the separations campaign for the Accelerator Transmutation of Wastes program that subsequently transitioned into the Advanced Fuel Cycle Initiative, the Global Nuclear Energy Partnership, and the current Fuel Cycle R&D Technology Program. Bill has remained as a key participant. His primary activities include the development of advanced processes for recovery and reuse of most of the components in used nuclear fuel, and research and development (R&D) on the processing of Gen IV reactor, TRISO-coated-particle fuel.

Over his nearly 30 years at ORNL, Bill's activities have included testing of UF₆ enrichment monitoring systems in support of the "Uranium Transparency Program", recovery and conversion of ²³³UF₆ to a stable form for long-term storage, remediation activities at the ORNL Molten Salt Reactor, R&D activities in high temperature molten salts, engineering studies of the disposition alternatives of the Defense Logistic Agency's thorium stockpile, and technical support related to the international weapons plutonium disposition program

Presently, Bill is a distinguished researcher in the Process Engineering and Research Group of the Nuclear Security and Isotope Technology Division, and is matrixed to the enrichment science and technology group supporting the American centrifuge program. He has participated in several National Nuclear Security Administration and Department of Homeland Security activities related to chemical signatures and observables in processes that could lead to the production of improvised uranium devices or clandestine enrichment facilities.

Conference Sponsorship

The conference organizing committee would like to thank the following organization for their sponsorship of this year's Actinide Separations Conference:



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May 24, 2016 (Tuesday - Morning)
Actinide Separations Plenary Session
Session Chair: James McNeese, Lawrence Livermore National Laboratory

8:00 AM	Welcome	James McNeese – LLNL
8:15 AM	The Search for New Elements – The Journey to Livermorium	Dawn Shaughnessy – LLNL
9:00 AM	Overview of LLNL Actinide Activities	Mark Bronson – LLNL
9:45 AM	Morning Break	BREAK
10:15 AM	Developing a Renewed Strategy for Used Fuel Recycle in the United States	Bill Del Cul – ONL
11:00 AM	Application of Industrial Perspectives to the Nuclear Fuel Cycle	Kevin Lyon – INL
11:25 AM	Theoretical prediction of coordination environments and stability constants of lanthanide lactate complexes in solution	Lindsay Roy – SRNL
11:50 AM	Lunch Break (until 1:30 PM)	BREAK

Developing a Renewed Strategy for Used Fuel Recycle in the United States

G. D. DelCul and E. D. Collins

Oak Ridge National Laboratory, 1 Bethel Valley Rd., Oak Ridge, TN 37831-6243

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Abstract

Nuclear power is the largest source of carbon-free energy in the USA (63%) producing large amounts of energy with very little fuel consumption by mass. One kilogram of uranium produces about 25,000 times more energy than one kilogram of a fossil fuel (coal or gas). In addition, more than 90% of the components in the used nuclear fuel (UNF) can be recovered and reused to produce even more energy, leaving behind a very small amount of waste. The recycling cost is relatively small (3 to 5 mills/kWh) and it may be lowered by advances in the recycling processes.

Public perception, when questions are framed in context, is somewhat favorable toward an expanded role for nuclear energy as a large and economical source of clean energy, except for the unresolved problem of what to do with the used nuclear fuel stockpile accumulating at the reactor sites and considered by some as a legacy of “nuclear waste” for future generations. Long-term interim storage, as recommended by the Blue Ribbon Commission, is a necessary and beneficial component of a sensible policy for used nuclear fuel, but not an end in itself.

Previous attempts to begin used fuel recycling in the United States have been challenged by contentions of (1) excessive costs, (2) proliferation concerns, (3) increased waste releases to the environment, and (4) future deployment of advanced reactors at unknown costs to be deployed in an undefined future. All of these factors contribute to the present status quo of indeterminate storage along with the slow demise of the U.S. leadership in nuclear technology.

Transitioning to a policy that allows and encourages used nuclear fuel to be recycled improves resource utilization, minimizes radioactive waste, and ensures that the United States can positively and effectively influence international fuel cycle decisions in the current era of expanded, global nuclear power deployment.

This paper will present alternatives for the practical, economical, and comprehensive recovery and recycle of the valuable components in used fuel while keeping in mind that no matter what approach is taken, successful implementation will require many decades of focused and sustained efforts over multiple administrations. This can only be achieved if guided by solid technical and economical bases that are widely supported.

Application of Industrial Perspectives to the Nuclear Fuel Cycle

Kevin L. Lyon, Mitchell R. Greenhalgh, Richard D. Tillotson, Melissa M. Warner
Idaho National Laboratory

The overarching goal of research and development activities related to the separation of minor actinides and lanthanides is the development of an efficient and economic integrated separation process. Various mineral processing industries utilize many unique separation techniques that may add perspective and value to challenging nuclear fuel cycle separations. For example, rare earth elements (REE) have received recent widespread attention because of their importance to advanced clean energy technologies, yet they are extremely difficult to separate economically and efficiently due to their chemical similarities. Recent efforts have investigated how innovative solvent extraction separation technologies indigenous to the nuclear industry may be used to improve REE separations. However, there are several solvent extraction practices unique to the REE industry that have not been explored for applications pertinent to the nuclear fuel cycle.

Various solvent extraction chemistries indigenous to the rare earth industry have been evaluated for various aqueous media systems including hydrochloric, nitric, sulfuric, and thiocyanate media for the separation of the minor actinides from the lanthanides. Additionally, rare earth extraction and stripping kinetics using PC88A have been evaluated to add perspective and insight to efforts related to complexation kinetics used in minor actinide/lanthanide separations. Kinetic data inherent to simple extraction chemistries helps inform flowsheet design and equipment selection for advanced separation processes.

One of the most unique techniques utilized in the rare earth industry involves the reflux of stripped product to facilitate metal-metal exchange when using liquid cation exchange ligands such as PC88A. This technique is used to facilitate the separation of adjacent rare earth elements that have extremely low separation factors, exploiting differences in ionic radii and charge density. For example, neodymium and praseodymium have an average separation factor of 1.5 in the PC88A/HCl solvent system, but co-extraction combined with reflux scrubbing techniques allows efficient separation of the adjacent elements. Interestingly, laboratory data suggests that metal reflux can also effectively scrub in solvating ligand chemistry systems under the proper loading conditions. In the present work, metal reflux scrubbing has been investigated for ²⁴¹Am and the lanthanides to develop a flowsheet process that selectively fractionates components similar to the approach utilized for rare earth separations.

Finally, integration of laboratory solvent extraction data to develop complete separation flowsheets remains a significant challenge, especially for new and innovative extraction chemistries. Solvent extraction models recently developed at the INL provide insight for bridging the gap between experimental data and process design. This work can potentially streamline the design and validation of new separation technologies relative to the nuclear fuel cycle.

Theoretical prediction of coordination environments and stability constants of lanthanide lactate complexes in solution

Lindsay E. Roy

Savannah River National Laboratory

Leigh R. Martin

Idaho National Laboratory

Understanding metal complexation in aqueous solution remains a formidable challenge for both experimental and theoretical chemists. While various computational methods are widely used in combination with experiments, it is still very difficult to accurately predict complex chemical phenomena, such as complex formation, computationally. The most detailed and realistic description of the solution environment involves inclusion of explicit solvent molecules and further treatment of solvent effects using molecular dynamics or Monte Carlo simulations. These types of simulations are not only computationally expensive and time-consuming, but also require extensive knowledge of the computational techniques. Conversely, continuum solvent models provide a simpler and more efficient approach to modeling solvation behavior by considering a dielectric constant surrounding the metal complex. While inexpensive, the approach does not offer the same rigor required for systems wherein extensive hydrogen bonding affects the overall structure. Therefore, there must exist a balance between the two methods that will simply and efficiently provide an accurate description of the metal complexation in solution. Our premise is that explicit solvent molecules are necessary to establish the proper structure, but that a continuum solvent model is appropriate for treating bulk solvent effects.

Using Density Functional Theory calculations in combination with explicit solvent and a continuum solvent model, this work sets out to understand the coordination environment and relevant thermodynamics of Ln(III)-lactate complexes. Calculations focus on the coordination modes for the complexes and changes in Gibbs free energy for complexation in solution. These results confirm that the α -hydroxyl group should be protonated, or at least hydrogen bonded to a water molecule, upon successive addition of the lactate ligand to the Ln(III) center using Bader's Atoms-in Molecules (AIM) approach. In addition, we present a straightforward method for predicting stability constants at the semi-quantitative level for Ln(III)-lactate complexes in solution. The proposed method could be particularly useful for prediction of lanthanide complex formation in various nuclear separations processes.

May 24, 2016 (Tuesday - Afternoon)
Session 1: Aqueous Processing and Oxide Characterization
Session Chair: Arfon Jones, AWE

1:30 PM	Announcements	
1:35 PM	Colloidal Co-extraction of Metals in the PUREX Process	Anna Baldwin – Colorado School of Mines
2:00 PM	Application of DGA Branched Resin for Separation of Ac and Ra from Proton Irradiated Th target and Lanthanides	Michael Fassbender – LANL
2:25 PM	Further Studies on the Behavior of Higher Valence Americium in Acidic Solution	Travis Grimes – INL
2:50 PM	Bench-Scale System for Preparing Plutonium Oxide Samples: Description and Initial Hot Run	Gregg Lumetta – PNL
3:15 PM	Afternoon Break	BREAK
3:35 PM	Surface Area, Particle Size Distribution and Thermal Analysis of Plutonium Oxides: Trends, Diagnostics, and Potential Forensic Applications	David Wayne - LANL
4:00 PM	LLNL Pu-238 Aqueous Recovery Operations in a Unique Glovebox	Michael Blau – LNLL
4:25 PM	An alternative approach to TALSPEAK chemistry using SO ₃ -Ph-BTP	Andreas Geist – Karlsruhe Institute of Technology (KIT)
4:50 PM	Break (until 6:30 PM)	BREAK

Colloidal Co-extraction of Metals in the PUREX Process

Anna G. Baldwin, Jenifer C. Braley
Colorado School of Mines

The Plutonium Uranium Redox Extraction (PUREX) process uses tributyl phosphate (TBP) to selectively extract uranium and plutonium from an aqueous feed consisting of irradiated nuclear fuel dissolved in molar nitric acid. The majority of fission and corrosion products remain in the aqueous phase during this separation, but some are slightly extracted in quantities dependent on the initial composition of the feed and process operating conditions. The low recovery of fission and corrosion products in PUREX has historically led to limited interest in unraveling the fundamental chemistry that drives their partitioning behavior. More recently, it has been suggested that the partitioning of trace metals could be relevant to pre-detonation forensic signatures.¹ Understanding the partitioning of trace metals under PUREX conditions would aid in the development of accurate PUREX process models that can be used to predict trace metal signatures for nuclear forensics applications.

Existing PUREX process models rely on empirical distribution values and aqueous phase activities to describe metal partitioning.² A more rigorous thermodynamic framework including the activities of organic phase species could provide better predictive performance with less data. Development of such a framework would require the inclusion and assessment of colloidal aggregation chemistry observed for TBP under conditions of high metal loading.³ Recent investigations of TBP aggregation chemistry have focused on the co-extraction by TBP of a single metal cation with water and nitric acid.⁴⁻⁶ The co-extraction of more than one metal cation has not been considered. Trace metal distribution studies of PUREX-like extraction systems completed at the Colorado School of Mines suggest that TBP co-extracts certain low valence transition metals with uranium. For example, contrary to expectations, the extraction of cesium increases with increasing uranium concentration. Diffusion NMR studies appear to support this observed trend. The diffusion coefficient of an extraction system containing uranium and cesium is smaller than that of a system containing uranium only, suggesting that cesium is extracted as part of the same complex as uranium. These results will be verified in future characterization of these systems using small angle scattering methods. Assessment of these systems will benefit the nuclear forensics community, while also providing insight into fundamental extraction mechanisms relevant to PUREX.

1. Moody, K. J.; Hutcheon, I. D.; Grant, P. M., *Nuclear Forensic Analysis*. CRC Press: 2005; pp 252-254.
2. Regalbuto, M. C.; Copple, J. M.; Leonard, R.; Pereira, C.; Vandegrift, G. F., Solvent extraction process development for partitioning and transmutation of spent fuel. In *8th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation*, Las Vegas, NV, 2004; pp 373-385.
3. Osseo-Asare, K., Aggregation, reversed micelles, and microemulsions in liquid-liquid extraction: the tri-*n*-butyl phosphate-diluent-water-electrolyte system. *Adv. Colloid Interface Sci.* **1991**, 37 (1-2), 123-173.
4. Chiarizia, R.; Nash, K. L.; Jensen, M. P.; Thiyagarajan, P.; Littrell, K. C., Application of the Baxter Model for Hard spheres with Surface Adhesion to SANS Data for the U(VI)-HNO₃, TBP-*n*-Dodecane system. *Langmuir* **2003**, 19 (23), 9592-9599.
5. Chiarizia, R.; Jensen, M. P.; Rickert, P. G.; Kolarik, Z.; Borkowski, M.; Thiyagarajan, P., Extraction of Zirconium Nitrate by TBP in *n*-Octane: Influence of Cation Type on Third Phase Formation According to the "Sticky Spheres" Model. *Langmuir* **2004**, 20 (25), 10798-10808.
6. Chiarizia, R.; Jensen, M. P.; Borkowski, M.; Thiyagarajan, P.; Littrell, K. C., Interpretation of Third Phase Formation in the Th(IV)-HNO₃, TBP-*n*-Octane System with Baxter's "Sticky Spheres" Model. *Solvent Extr. Ion Exch.* **2004**, 22 (3), 325-351.

Application of DGA Branched Resin for Separation of Ac and Ra from Proton Irradiated Th target and Lanthanides

Valery Radchenko¹, Catherine A. Meyer¹, Roy Copping², Justin J. Wilson¹, Jonathan W. Engle¹, Karen Murphy², David Denton², Justin R. Griswold², Jonathan M. Fitzsimmons³, Eva R. Birnbaum¹, Leonard F. Mausner³, F. Meiring Nortier¹, Kevin D. John¹ and Michael E. Fassbender¹

¹Los Alamos National Laboratory, Los Alamos, NM, USA

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Targeted alpha therapy (TAT) is an effective treatment method for neoplasms. The main limitation for TAT is the availability of alpha particle emitting radionuclides with nuclear and chemical properties conducive to TAT treatment regimens. High energy proton irradiation of thorium targets results in the formation of several alpha particle emitting radionuclides with potential as therapeutic agents (e.g. ²²⁵Ra/²²⁵Ac/²¹³Bi, ²³⁰Pa/²³⁰U/²²⁶Th, ²²⁷Th/²²³Ra etc.). Such radionuclides need to be chemically recovered from the bulk thorium mass and purified from co-produced fission products. In our previous work [1,2] we proposed a two-step procedure for the isolation of ²²⁵Ac and ^{225/223}Ra. One of the steps described therein includes the use of branched DGA resin to separate Ac and Ra/Ba from radiolanthanides (e.g. ¹⁴⁰La, ^{141,143}Ce). In order to shed more light on the underlying mechanism of the observed Ln/Ac separation effect, we further studied the sorption behavior of lanthanides Ce, Eu and Lu in the system DGA/HNO₃. Separation experiments with 185-370 MBq (5-10 mCi) of ²²⁵Ac, ^{225,223}Ra, Ba and radiolanthanide activities were conducted, and several lanthanides were contacted with BDGA resin in HNO₃ matrices of various concentrations to investigate elution behavior. Additionally, the distribution behavior of Th(IV) was tested.

Scale up experiments showed applicability of this method for bulk processing; no radionuclide contaminants were detected in the final Ra/Ba and Ac fractions. Thorium was retained on the BDGA resin throughout the whole process, which provided additional fine purification from the target material. All lanthanides were strongly retained on the BDGA resin in 10M HNO₃, while ²²⁵Ac eluted quantitatively under this condition. No detectable breakthrough of lanthanides was observed in the eluted Ac fraction (10 M HNO₃). After additional resin washes with 50 bed volumes of 10, 12 and 14 M HNO₃, no lanthanides were detected in the washes; lanthanides could then be desorbed using 0.1M HNO₃. We conclude that the BDGA/HNO₃ sorption system can be effectively employed for the separation of Ac and Ra from fission product radiolanthanides and residual Th mass in order to yield high purity medical ²²⁵Ac for TAT applications.

Acknowledgments: This material is based upon work supported by the United States Department of Energy, Office of Science, Office of Nuclear Physics, via an award from the Isotope Development and Production for Research and Applications subprogram, and by the Los Alamos Laboratory Directed Research and Development (LDRD-ER) Program.

- 1) Radchenko, V.; Engle, J.W.; Wilson, J.J.; Maassen, J.R.; Nortier, F.M.; Taylor, W.A.; Birnbaum, E.R.; Hudston, L.A.; John, K.D.; Fassbender, M.E. Application of ion exchange and extraction chromatography to the separation of actinium from proton-irradiated thorium metal for analytical purposes. *J. Chromatography A* **2015**, *1380*, 55-63.
- 2) Radchenko, V.; Engle, J.W.; Wilson, J.J.; Maassen, J.R.; Nortier, F.M.; Birnbaum, E.R.; John, K.D. and Fassbender, M.E. Formation cross-sections and chromatographic separation of protactinium isotopes formed in proton-irradiated thorium metal, *Radiochim Acta*, **in press**.

Further Studies on the Behavior of Higher Valence Americium in Acidic Solution

Travis S. Grimes^{}, Masahiko Nakase[†], Nicholas C. Schmitt^{*} and Bruce J. Mincher^{*}*

^{*}Aqueous Separations and Radiochemistry, Idaho National Laboratory

[†]Actinide Chemistry, Quantum Beam Science Center, Japan Atomic Energy Agency

Group actinide separation by oxidation of Am(III) remains a promising pathway for simplifying previously proposed solvent extraction processes. The oxidation of Am(III) to Am(VI) would reduce the number of steps necessary to recycle used fuel by incorporating a group actinide decontamination where U, Pu, Np, and Am are co-extracted as linear dioxo cations in one step, and then selectively back extracted into appropriate product streams. The oxidation of Am(III) to Am(VI) is conducted using sodium bismuthate because it is proven to be the most effective oxidant when Am(VI) is contacted with an organic phase. Previous studies have shown the zero order reduction rates for Am(VI) are unaffected by acid concentration or total americium concentration in the system. In this study we continue to build our understanding of Am(VI) reduction by measuring these rates in the presence of Ce⁴⁺, under static gamma irradiation, and in the organic phase as the extracted complex with diamylamylphosphonate (DAAP). This presentation will also highlight work done in collaboration with the Japan Atomic Energy Agency conducted at INL.

Bench-Scale System for Preparing Plutonium Oxide Samples: Description and Initial Hot Run

Gregg J. Lumetta, David E. Meier, and Joel M. Tingey

Pacific Northwest National Laboratory

The National Technical Nuclear Forensics Center (NTNFC) within the Domestic Nuclear Detection Office (DNDO) of the Department of Homeland Security (DHS) has funded Pacific Northwest National Laboratory (PNNL) to establish a bench-scale (up to 10 g Pu per batch) capability to synthesize plutonium oxide (PuO_2) for use in identifying and validating nuclear forensics signatures associated with plutonium processing. The bench-scale system has been established in a series of gloveboxes, and its functionality was demonstrated with plutonium obtained from in-house stocks at PNNL. The following unit operations are included in the bench-scale system: 1) dissolution of as-received PuO_2 , 2) purification of the Pu nitrate solution by anion exchange, 3) concentration of the purified Pu nitrate solution by evaporation, 4) Pu(III) oxalate precipitation, and 5) thermal conversion of the Pu(III) oxalate to PuO_2 . This paper will describe the initial experience of operating this system, along with preliminary characterization of the product materials *via* scanning electron microscopy, thermal gravimetric analysis, and diffuse reflectance UV/visible spectroscopy.

Surface Area, Particle Size Distribution and Thermal Analysis of Plutonium Oxides: Trends, Diagnostics, and Potential Forensic Applications (LA-UR-16-22753)

David M. Wayne

MET-1, Los Alamos National Laboratory

Much of the effort within the nuclear forensics community implements trace element and isotopic signatures of special nuclear materials (SNM) combined with well-constrained assumptions about process history to determine the age and likely origin of interdicted materials. Despite the utility of chemical tracers, forensic studies are necessarily multi-disciplinary, as samples may be impure and the amount available for analysis may be small. No single analytical technique has thus far provided an un-ambiguous and unique attribution signature. The ubiquity of PuO₂ in the worldwide nuclear complex is attributable to its great stability. Sintered actinide oxide pellets are the dominant fuel form in nuclear reactors, and power generators have investigated mixed Pu and U oxide fuels. In large-scale processes, PuO₂ is generated by a variety of methods; calcination of oxalate precipitates, heating the metal in air or an oxygen-rich gas stream. Actinide oxides, mixed with a characteristic assemblage of actinide bearing salts and other compounds, are common by-products of reprocessing activities in both the weapons and nuclear power arenas.

In recent years, nuclear forensic investigations have turned to particle characterization to help ascertain the history and provenance of interdicted materials. Particle morphology can be diagnostic for oxalate-precipitated PuO₂ because crystal morphological characteristics are known to vary in response to changes in solution temperature and chemistry^[1]. These properties are passed on to the PuO₂ product. Collectively, such observations form the basis for comprehensive particle morphology datasets which can be used to determine the processing history of some actinide oxide particulates^[2,3]. In addition to particle morphology studies, the measurement of other physical characteristics--such as particle size distribution (PSD), specific surface area (SSA), and thermal behavior (TGA-DSC)--has been performed at the Los Alamos National Laboratory (LANL) for several decades. Early on, investigators observed systematic variations in optical properties, SSA, PSD, and the bulk and tapped density of PuO₂ aggregates and powders produced by different methods^[4,5]. They also observed that changing process parameters may systematically alter the physical properties of the resulting product.

The intent of this talk is to examine the utility and applicability of PSD, SSA, TGA-DSC, and offgas analysis in the nuclear forensic arena. Oxide production at LANL has involved both oxalate precipitation and controlled metal burning. Thermal analysis, SSA, and PSD data for oxides generated by different TA-55 PuO₂ process lines shall be presented and evaluated from a forensics standpoint.

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- 2) Tamasi, A.L.; Cash, L.J., and 10 others, A lexicon for consistent description of material images for nuclear forensics. *J. Radioanal. Nucl. Chem.* **2016**, 307(3), 1611-1619.
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LLNL Pu-238 aqueous recovery operations in a unique glovebox line (U)

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The purpose of this work was to demonstrate that a corrosion resistance modular glovebox line could be used for Pu-238 aqueous recovery operations and sized such that each module would fit within a standard TRUPACTII Waste Box that could be sent to WIPP, instead of the tremendous cost of deconing the glovebox, to low-level. LLNL designed, fabricated, and installed, a modular line consisting of three hastelloy C22X and two stainless steel kynar coated gloveboxs. The modular line has been used to successfully separate Pu-238 from beryllium for a few years with no glovebox corrosion issues. For the last few years the Pu-238 separation mission has increased. Also, the line was used to demonstrate Pu-238 purification using ion exchange from Pu with high concentration of U-234 from ingrowth.

LLNL-ABS-690598

An alternative approach to TALSPEAK chemistry using SO₃-Ph-BTP

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The TALSPEAK process was developed over 50 years ago for separating actinides(III) from lanthanides(III) by solvent extraction. Over the last decade scientific interest in this process has revived. To handle some of its disadvantages such as a narrow pH window, a largely improved process, ALSEP, has been developed in the US.

The idea behind TALSPEAK—masking actinides(III) in the aqueous phase to make them less extractable than the lanthanides(III)—has also been exploited in recent European research programmes, ACSEPT and SACSESS. However, rather than using polyaminocarboxylates, a water soluble bis-triazinyl-pyridine, SO₃-Ph-BTP, is utilised to strip actinides(III) from a TODGA solvent loaded with actinides(III) and lanthanides(III). Excellent selectivity for actinides(III) over lanthanides(III) is achieved and the stripping of actinides(III) is performed around 0.5 mol/L HNO₃.

We first tested SO₃-Ph-BTP as a stripping agent for actinides(III) about five years ago. In the meantime, two separation processes using SO₃-Ph-BTP have been developed and lab tested: an i-SANEX process, separating Am(III) and Cm(III) from PUREX raffinate, and a GANEX 2nd cycle process, separating Np(VI), Pu(IV), Am(III) and Cm(III) from a GANEX 1st cycle (equivalent to UREX) raffinate.

After confirming the good chemical stability of SO₃-Ph-BTP, a concept for separating the actinides from SO₃-Ph-BTP and recycling the latter has been devised. Unfortunately, SO₃-Ph-BTP is susceptible to radiolytic damage, challenging its recyclability under process conditions. Owing to its sulphur content, secondary waste is generated upon degradation.

This contribution is intended to give an overview of what so far has been achieved with SO₃-Ph-BTP, highlighting its advantageous properties while not denying its drawbacks, and pointing out possible future development.

The research leading to these results is being performed in the SACSESS project funded by the European Atomic Energy Community Seventh Framework Programme under grant agreement No. 323282.

May 24, 2016 (Tuesday - Evening)
Poster Session

Session Chair: Kiel Holliday, Lawrence Livermore National Laboratory

P01	Dissolution of Used Nuclear Fuels at SRS using Waste Solutions from HB-Line Anion Exchange	Philip Almond – SRNL
P02	Extraction Kinetics and Hydrodynamics in Miniature Annular Centrifugal Contactors	Tro Babikian – UC Irvine
P03	Uranium and Rare Earth Recovery from Phosphoric Acid Production	Derek Brigham – ORNL
P04	Complexation And Extraction Studies Of High Valency Actinides By Schiff base-ligands	Christian Bustillos, UC Irvine
P05	Separation and Quantification of Thorium by UV-VIS Spectrophotometry in Heat Source Plutonium	Nell Carver, LANL
P06	Plutonium Metal Conversion Technology and Equipment Upgrades	Paul DeBurgomaster – LANL
P07	Moisture Measurements for Plutonium and Neptunium Oxides to Support Safe Packaging, Transportation, and Storage	Jonathan Duffey – SRNL
P08	Pyrochemical treatment of spent salts by oxidation and vacuum distillation process	Stephanie Dumontet – CEA
P09	Mechanics of Millifluidic and Microfluidic Plutonium Separation Processes	Kyle Gardner – LANL
P10	HYDOX Technology at LLNL	Greg Gdowski – LLNL
P11	Equilibria involved in the extraction of An(III), Ln(III) and HNO ₃ by a TODGA solvent	Andreas Geist – Karlsruhe Institute of Technology (KIT)
P12	Investigation of the Nucleation and Growth of Eu(III) Oxalate Crystals	Gabriel Hall – PNL
P13	Beryllium Oxide Sparge Tube Experiment in Pyrochemical Plutonium Operations	J. Matt Jackson – LANL
P14	Investigating the Precipitate Filtration System for the 3013 Can Electrolytic Decontamination System	Susan Klimowicz – LANL
P15	Evaluation of Polyvinyl Chloride Bags during Plutonium Storage	Lucas Kyriazidis – SRNL

P16	Understanding the Range of Safe Wash Acid Concentration for Pu Anion Exchange Columns	Eddie Kyser – SRNL
P17	Radiolytic degradation of solvent extraction ligands in the presence of UO ₂ ²⁺ metal Ions	Randy Ngelale – UC Irvine
P18	Particulate Separation from the Outlet of Plutonium Pyrochemical Processes	David Parkinson – LANL
P19	Lab-scale Testing of a Codecontamination Process	Candido Pereira – PNL
P20	Purification of ²²⁹ Th for measurement of nuclear isomeric transition at LANL	Valery Radchenko - LANL
P21	Determination of Pu Isotopic Abundances Using an Alpha Spectrum Peak Fitting Algorithm	Jung Ho Rim – LANL
P22	Ion-Exchange Based Separation of Americium	Thomas Shehee – SRNL
P23	Infrastructure Improvement for Analytical Chemistry and Materials Characterization Capabilities at Los Alamos National Laboratory	Louis Shulte – LANL
P24	Characterization of f-element oxide stoichiometry and phases through Raman Spectroscopy	Jared Strizinger – LANL
P25	Hydrogen Generation in Aqueous Tanks at the LANL Plutonium Facility	Mary Ann Stroud
P26	Silica-Salophen Hybrid Material for Uranium Sequestration	Jaclynn Unangst – UC Irvine
P27	Mitigation of Chloride Contamination in the Plutonium Feed Stream for Aqueous Nitrate Processing	Crestina Vigil & Yvonne Martinez – LANL
P28	Quantifying TBP dimers and trimers in alkane solutions via Simulations and Experiments	Quynh Vo – UC Irvine

Dissolution of Used Nuclear Fuels at SRS using Waste Solutions from HB-Line Anion Exchange

P. M. Almond, W. E. Daniel, and T. S. Rudisill

Savannah River National Laboratory

Minimization of the liquid waste volume generated during operations at the SRS H-Canyon and HB-Line facilities has been a major initiative due to a reduced capacity to process waste in the H-Area tank farm. To reduce the volume of waste generated in the HB-Line facility from the production of PuO₂, SRNL was tasked to develop a flowsheet for the dissolution of used nuclear fuel (UNF) using waste solutions from the HB-Line anion exchange process, as a substitute for clean nitric acid. The UNF to be processed in H-Canyon includes foreign and domestic research reactor fuels. These fuels are typically uranium-aluminum alloys with aluminum cladding.

The waste solutions from the HB-Line anion exchange process consist of 7-7.5 M nitric acid from column reconditioning, raffinate, wash, and head/tails cuts. Impurities in the solutions include: iron, chromium, nickel, manganese, aluminum, potassium, fluoride, chloride, boron, americium, and plutonium.

A series of small-scale laboratory experiments was performed using aluminum and uranium-aluminum alloy coupons to model the dissolution of the aluminum charging bundle and uranium-aluminum alloy fuel. A mercury catalyst concentration of 0.002 to 0.012 M was used during the dissolutions. Generally, four, 1.5-2.0 g coupons were sequentially dissolved in a simulated dissolving solution targeting final aluminum and nitric acid concentrations of 1.7 M and 0.5 M, respectively. Gas samples were collected during each experiment and analyzed for hydrogen. Results from the experiments will be discussed including the controls necessary to prevent exceeding 60% of the lower flammability limit of hydrogen in the H-Canyon dissolver offgas.

- 1) P. M. Almond, W. E. Daniel, and T. S. Rudisill, "Flowsheet Modifications for the Use of AFS-2 Column Waste in Used Nuclear Fuel Dissolutions," SRNL-STI-2014-00045, September 2014.

Extraction Kinetics and Hydrodynamics in Miniature Annular Centrifugal Contactors

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Annular centrifugal contactors have become attractive equipment in the recycling process of spent nuclear fuel for their high efficiency, throughput, and rapid operational properties. Various sizes of contactors ranging from laboratory scale to commercial scale have been manufactured for different needs and process scales, possibly allowing us to study the scaling effects on the extraction efficiency. The Robatel BXP012 is a lab scale French made contactor with a 12mm inner rotor diameter. In this study, the residence time of both the aqueous and the organic phases has been measured using residence time distribution analysis with a pulse input consisting of $\text{Dy}(\text{NO}_3)_3$ in the aqueous phase and CMPO in the organic phase. The measured values proved not to reflect the residence time of the phases inside the mixing zone due to the relatively large collection rings. RPM, phase continuity, and flow rate effects on the extraction efficiency have also been investigated in this study. It was noted that the condition of aqueous continuous at 4500 RPM was operationally favorable.

Uranium and Rare Earth Recovery from Phosphoric Acid Production

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The rare earth elements (REEs) are considered critical materials due to their use in clean energy technologies, and concerns over supply challenges for REEs have caused renewed interest in developing alternate sources of production. One such source is the REE content found in the phosphate rock that is mined for phosphoric acid production. There is an established history of industrial scale material recovery out of phosphoric acid production as uranium was extracted from wet process phosphoric acid starting in the 1950's through the late 1990's using solvent extraction techniques. Combining the recovery of uranium with that of the REEs out of phosphoric acid production is an attractive, potentially economically viable option. This work presents the extraction of uranium and REEs from wet process phosphoric acid employing synergistic solvent extraction systems. Results from bench-scale mixer-settler trials with industrial acid samples show good extraction of REE and U while reducing the impact of interfacial crud formation.

Research funded by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

Complexation And Extraction Studies Of High Valency Actinides By Schiff base-ligands

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Increased knowledge of actinide coordination chemistry and the development of advanced actinide separation processes are essential to reducing the radiotoxicity of used nuclear fuel. Commercial separation techniques for nuclear fuel have focused on the selective extraction of U(VI) and Pu(IV), however, contemporary efforts are aimed at extracting the minor actinides, e.g. Np and Am. These four mid-actinides (U, Np, Pu, Am) have accessible oxidation states (+V, +VI) at which they exist as linear dioxo actinyl ions $[\text{AnO}_2]^{n+}$, offering the possibility of co-extraction of all 4 actinide cations. The $\text{An}=\text{O}$ bonds permit ligand coordination in the equatorial plane of the metal ion center, affording a geometry for unique bonding characteristics. Schiff bases can be prepared with synthetic ease and have rather planar structures that chelate around the equatorial plane of actinyl ions through their N_2O_2 binding site, presenting the possibility that this distinct coordination environment may facilitate the selective solvent extraction or aqueous retention of pentavalent and hexavalent actinides. Preliminary results indicate that these ligands show great promise for group extraction or retention of the mid-actinides in a biphasic solvent extraction process. Lipophilic salen-based ligands prepared in our lab are able to extract uranium from a slightly acidic nitrate media with 90% or higher extraction in one contact, and also demonstrated the ability to extract uranium in the presence of Dy^{3+} and EDTA with a $D_{\text{U}}=1.63$ and a $\text{SF}_{\text{U/Dy}}=2037$. These ligands have been shown to form 1:1 complexes UO_2^{2+} , NpO_2^{2+} and PuO_2^{2+} which have been structurally and spectroscopically characterized. Recent results from our ongoing study will be presented and discussed.

LA-UR-16-22698

Separation and Quantification of Thorium by UV-VIS Spectrophotometry in Heat Source Plutonium

Nell Carver

Los Alamos National Laboratory

Thorium-232 has historically been measured in heat source plutonium ($^{238}\text{PuO}_2$) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the Chemistry and Metallurgy Research (CMR) building at Los Alamos National Laboratory (LANL). With the impending closure of CMR, all heat source plutonium analytical chemistry operations have been moved to the LANL Plutonium Facility.

Analytical Chemistry capabilities in the Plutonium Facility do not include an ICP-MS therefore an alternative method to determine thorium in heat source Pu by DC (Direct Current) Arc Spectrometry was developed. Thorium is difficult to measure by DC Arc since it is an actinide and behaves similarly to the plutonium matrix and it has many emission lines but none of significant intensity. Detection limits for thorium by DC Arc are in the 100-500 ug Th/g $^{238}\text{PuO}_2$ range and percent relative standard deviations (%RSD) are large, sometimes up to 50%.

Radiochemistry counting techniques such as alpha spectrometry and gamma spectrometry are difficult since Th-232 is the longest lived ($T_{1/2} = 14$ billion years) and most stable isotope of thorium.

In order to improve the detection limit and precision a new method for thorium determination was developed based on a longstanding Arsenazo III Spectrophotometric method. The new method uses an Eichrom TEVA® column to separate thorium from the $^{238}\text{PuO}_2$ matrix. The thorium is eluted in 4M hydrochloric acid, ascorbic acid is added to reduce any residual Pu to Pu(III), and Arsenazo III is added to form a colored complex with thorium. Thorium is determined photometrically using a scanning UV- Visible spectrophotometer at 665 nm.

Additional experiments were carried out to ensure Pu(IV) and Np(IV) were not present in the sample as interferences. Results show that detection limits are significantly improved over DC Arc, with the UV- VIS detection limit being 50 ug Th/g $^{238}\text{PuO}_2$. Replicate data show that precision is better than 5%.

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Plutonium Metal Conversion Technology and Equipment Upgrades

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Conversion of hundreds of kilograms of plutonium primary “pits” to plutonium oxide has primarily been produced at Los Alamos National Laboratory. Continuous processing via Direct Metal Oxidation (DMO) modules has converted hundreds of kilograms of metal to oxide. Batch processing through muffle furnace air oxidation has produced on the order of 10kg of plutonium oxide. Equipment and technology upgrades will be discussed for both oxidation approaches as well as characteristics of the resultant products.

LA-UR-16-22958

**Moisture Measurements for Plutonium and Neptunium Oxides to
Support Safe Packaging, Transportation, and Storage**

Jonathan M. Duffey
Savannah River National Laboratory

Due to the potential for gas generation from water radiolysis, knowledge of the moisture content of radioactive materials such as plutonium and neptunium oxides is needed to safely package these materials in sealed containers. For transportation and storage applications the moisture content of these oxides is typically required to be less than 0.5 wt % to mitigate potential flammable gas generation and pressurization concerns. For more than 10 years the Savannah River National Laboratory (SRNL) has performed moisture measurements of plutonium and neptunium oxides by thermogravimetric analysis with mass spectrometry (TGA-MS) in support of oxide production campaigns and for material characterization during the destructive examination of plutonium oxide storage containers. This presentation will discuss the methodology used at SRNL, factors that affect the moisture content of plutonium and neptunium oxides, and factors important to obtaining an accurate moisture measurement.

Pyrochemical treatment of spent salts by oxidation and vacuum distillation process

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Plutonium pyrochemical processing has generated spent salts. Most of these salts consist of chlorides - equimolar NaCl/KCl and NaCl/CaCl₂ mixtures - containing various plutonium and americium species with oxidation state varying from 0 to IV (metal, chlorides, oxichlorides and oxides), resulting from process operating conditions and from interim storage environment. A pyrochemical treatment is developed in the frame of residue treatment programs. The flowsheet includes three steps : oxidation, chlorination and vacuum distillation.

Oxidation-chlorination (so called pyro-oxidation) aims to convert easily vaporizable Pu and Am species into stable actinides oxides (PuO₂ and AmO₂). Two phases are obtained: a top clean product which contains about 60 %wt of the initial alkali or alkaline earth chlorides solvent with a low actinides content and a bottom precipitate which contains almost totality of actinide oxides.

The final chlorides/oxides separation is carried out by vacuum distillation. Tests with NaCl/KCl and NaCl-CaCl₂ active oxidized spent salt give decontamination factor higher than 2000. The distillate salts meet the radiologic requirement to be discarded as low level waste.

The chloride-free oxides obtained by vacuum distillation can be dissolved in nitrofluoric acid at 80°C (more than 94% yield) for further aqueous nitrate processing.

Mechanics of Millifluidic and Microfluidic Plutonium Separation Processes

Kyle S. Gardner

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Potential institution of milli- and microfluidic aqueous processing systems at Los Alamos National Laboratory could result in a drastic footprint reduction for Plutonium recycle and recovery operations. Benefits to such a reduction include a decrease in waste generation, decreased worker exposure, increased availability of process floor space, and alleviation of nuclear criticality safety concerns. A strong understanding of the effect of flow parameters and material properties on the fluid mechanics of these systems is key to developing models capable of accurately predicting process performance. To this end, hydrodynamic studies have been performed on milli-scale, biphasic flows of two immiscible liquids (Aliquat-336 and aqueous HCl solution) through circular, hydrophobic tubing.

A brief overview of the milli/microfluidic liquid-liquid extraction process will be given, with an emphasis on the major fluid mechanics principles involved. Efforts to study and model the effects of flow configuration, fluid concentrations, viscosity, surface tension, mass transfer, and flow rate will be presented. Finally, the next steps toward further understanding of milli/microfluidic systems in the context of Plutonium separations will be discussed.

HYDOX Technology at LLNL

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Hydride Oxidation (HYDOX) technology developed and implemented at Lawrence Livermore National Laboratory (LLNL) is used to convert plutonium and/or uranium metal to oxide using hydride and nitride intermediates. The process proceeds in the following conversion steps

Metal -> Hydride -> Nitride -> Oxide

The advantage of using the hydride intermediate is that it allows the plutonium and/or uranium to be separated from comingled bulk items that do not form hydrides prior to the oxidation step. The hydride powder is easily separated from the non-hydride material by sieving.

The advantage of using the nitride intermediate is that it allows physical separation and isolation of the processes with hydrogen and oxygen. Thus mitigating the hazards associated with hydrogen-oxygen reactions.

The HYDOX technology has been used to process two types of Zero Power Physics Reaction (ZPPR) fuel, Pu-depleted U-Mo and Pu-Si. Processing equipment and processing parameters have been optimized to minimize hydrogen use, processing time, and oxide product.

LLNL-ABS-691560

Equilibria involved in the extraction of An(III), Ln(III) and HNO₃ by a TODGA solvent

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TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) and other diglycolamide (DGA) compounds are used to extract actinide and lanthanide ions from nitric acid solutions. Different DGA based solvents have been developed and utilised for actinide separations, mainly in Japan, India, USA and in Europe. A solvent containing 0.2 mol/L TODGA and 5% 1-octanol in kerosene is the European reference solvent.

We have determined distribution data for the extraction of trivalent actinide and lanthanide ions and nitric acid over a range of nitric acid concentrations (0.1–5 mol/L), TODGA concentrations (0.05–0.3 mol/L) and temperatures (10–50°C). Based on these data, an equilibrium model was developed.

Nitric acid extraction is described by (HNO₃)(TODGA)₂, (HNO₃)_{1–4}(TODGA), (HNO₃)(1-octanol)_{1–3} and (HNO₃)_{0–4}(TODGA)(1-octanol) complexes. The temperature dependence is described by a value of $\Delta G = -20.7$ kJ/mol.

The extraction of actinide and lanthanide ions (M = Am(III), Cm(III), Y(III) and La(III)–Lu(III)) is described by the formation of M(NO₃)₃(HNO₃)_{0–2}(TODGA)_{2–3} complexes, as evident from slope analysis and numerical fitting of extraction data, further supported by organic phase saturation experiments. The major species shift from complexes containing three TODGA molecules for Am(III) and the light Ln(III) to complexes containing two TODGA molecules for the heavy Ln(III). Extraction is exothermic. The temperature dependence of Am(III), Cm(III) and Ln(III) extraction is described by the following thermodynamic data, $\Delta G = -(78–94)$ kJ/mol. The presence of three TODGA molecules and the absence of water in the first coordination sphere was verified for Cm(III) and Eu(III) by time resolved laser fluorescence spectroscopy (TRLFS).

To provide a more general applicability of these data, the influence of different diluents (three different kerosenes and *n*-dodecane) on Am(III) and nitric acid extraction was checked. No significant effect of the diluent on the amount of nitric acid extracted was observed. However, Am(III) distribution ratios differ by a factor of 1.5 between the largest and the smallest distribution ratios.

The research leading to these results is being performed in the SACSESS project funded by the European Atomic Energy Community Seventh Framework Programme under grant agreement No. 323282.

Investigation of the Nucleation and Growth of Eu(III) Oxalate Crystals

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Actinide oxides, which see use in the nuclear fuel industry, are produced through precipitation with oxalate, and subsequent calcination. Due to the potential for actinide oxalate morphology to effect characteristics of the produced oxides this area has recently been under investigation in the literature.^{1,2} The present study is using europium as a non-radioactive model and aims to study changes in europium oxalate crystals with respect to crystallization conditions. This includes investigating the fundamental science behind the nucleation process. Kinetics of nucleation, and structural changes associated with changes in reactant concentrations as well as the concentration of other chemical species in solution (e.g. HNO₃) are examined by X-ray diffraction (XRD) scanning and tunneling electron microscopies (SEM and TEM), infrared and fluorescence spectroscopies, and computational modeling.

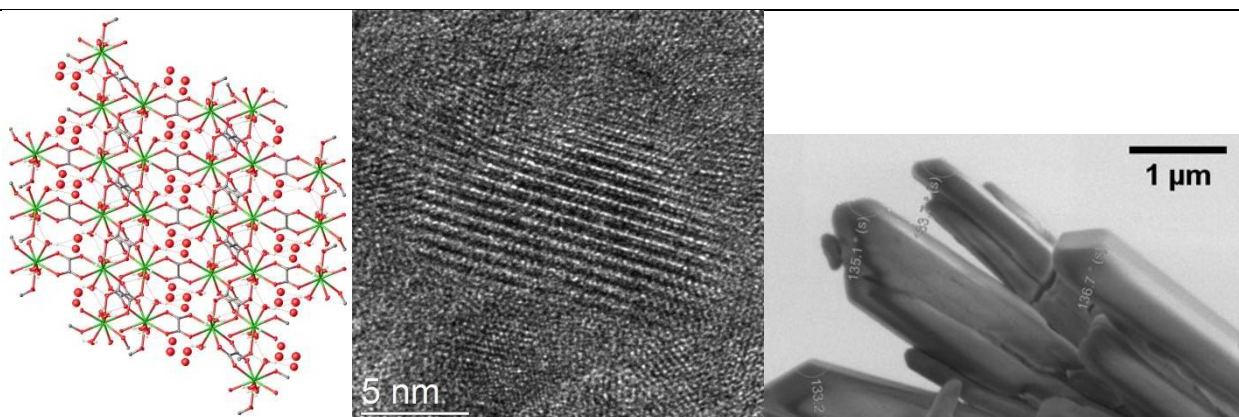


Figure 1. From left to right: single crystal XRD structure of europium oxalate as viewed along the b-axis, TEM of europium oxalate crystal, SEM of europium oxalate crystals.

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- 2) Runde, W.; Neu, M. P.; Van Pelt, C.; Scott, B. L. *Inorg. Chem.* 2000, 39, 1050–1051

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Ceramic sparge tubes are used in several plutonium metal production processes at Los Alamos National Laboratory. The sparge tube is the delivery method for the anhydrous chlorine gas utilized in the Direct Oxide Reduction (DOR), Americium Extraction (MSE), and PuCl_3 Generation processes. The DOR process reduces plutonium oxide to plutonium metal using calcium metal. The reaction takes place at 850 C in a molten calcium chloride solvent salt. The byproduct of the reaction is calcium oxide, a reaction poison, which is then converted back to calcium chloride by sparging with chlorine gas which allows multiple reductions to be performed under a single heat cycle. The salt-less MSE process sparges chlorine gas into molten plutonium metal at 850 C for a short period of time in order to extract americium from the plutonium metal. PuCl_3 and AmCl_3 salts are formed and float to the top of the melt. Americium is a less noble metal than plutonium and is therefore more readily converted into a salt. PuCl_3 is used as a seeding reagent in the plutonium electro-refining process, and is generated by chlorinating purified plutonium for an extended period of time. Currently Magnesium Oxide (MgO) sparge tubes are used for the delivery of chlorine gas to the processes discussed above. Many problems have been found to exist with the MgO sparge tubes. MgO is not a very well suited material for the high temperature plutonium/chlorine environment. Particularly in the metal chlorination processes sparge tubes are rapidly deteriorating. The rapid deterioration increases the chances of a costly failed run. In addition to their chemical instability MgO sparge tubes were susceptible to failure either by thermal shock, or worker mishandling (fragility).

Beryllium oxide or beryllia is advantageous over magnesium oxide for several reasons. The first being beryllia's unique thermal properties. Beryllium oxide has a thermal conductivity of $330 \text{ WK}^{-1}\text{m}^{-1}$ and a coefficient of thermal expansion of 6.5×10^{-6} (at room temperature). Magnesium oxide has a thermal conductivity of $45 \text{ WK}^{-1}\text{m}^{-1}$ and a coefficient of thermal expansion of 10.4×10^{-6} (at room temperature). Therefore the BeO sparge tube would be much less susceptible to failure due to thermal shock. Additionally the beryllium oxide ceramic is much more durable than the magnesium oxide. The Knoop hardness of BeO is 2000 while MgO has a Knoop Hardness of 692. Over the expected service temperature range beryllium oxide has a lower Gibbs free energy than does magnesium oxide. This is an indication that beryllium oxide is a more stable ceramic for the processes operating temperature range.

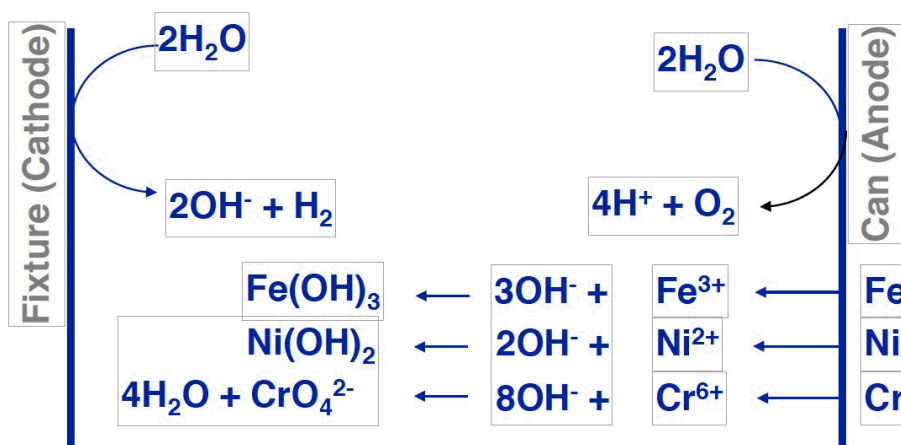
(LA-UR 12-01649)

Investigating The Precipitate Filtration System For The 3013 Can Electrolytic Decontamination System

Susan Klimowicz, Jane Lloyd, Kenny Hansel, Kirk Weisbrod

The Advanced Recovery Integrated Extraction System (ARIES) employs an electrolytic decontamination system to remove contamination from the outside surfaces of the inner 3013 containers. The process, which removes about a micron from the outside of the container, is an electrochemical technique that produces a precipitate entraining the small amounts of surface actinide contaminants, acquired from exposure to the glovebox line. A more efficient filtration model to replace or improve the filtration of the residue from reusable electrolyte is being investigated. The current system utilizes a pump to transport the electrolyte solution from its reservoir tank into a basic filter boat allowing the separation of the solution and precipitate. Specific-cake resistance, filter-medium resistance, time, and flow rate were used to evaluate three different filtration systems.

The comparisons of the filtration systems will be presented for the electrolytic decontamination system.



SRNS-TR-2016-00097

Evaluation of Polyvinyl Chloride Bags during Plutonium Storage

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Abstract

Plutonium separation processes encompass a wide range of topics, ranging from plutonium chemistry to environmental effects during handling and storage of the material. Packaging, handling, and storage of plutonium materials are important processes having a tremendous impact on any plutonium separations strategy. Gas generation and moisture adsorption are key effects that must be accounted for during the interim storage of plutonium.

Plutonium materials are stored in 9975 shipping packages at the Savannah River Site (SRS). One configuration that plutonium materials are packaged in is a can-bag-can configuration within the 9975 shipping package. The cans are made of stainless steel and are filtered to allow for hydrogen diffusion. The inner can is a slip lid container. The plutonium is packaged in the slip lid container in a glove box, the slip lid is taped, and the can is bagged out in a filtered plastic bag. The bagged can is then placed into a filtered screw-lid container. The 9975 is allowed up to 100 grams of plastic during shipping, with an acceptable type of plastic used for the bag and tape being plasticized polyvinyl chloride (pPVC).

Plasticized PVC is known to degrade by thermal and radiolytic mechanisms. This evaluation identifies the onset for thermal degradation of pPVC bags and tape during storage of the 9975 shipping package to align with a 7 Watt heat load. The evaluation also very conservatively determines the maximum pressure within the 9975 Primary Containment Vessel (PCV) to be approximately 156 psig (well under the design pressure of the PCV) for a heat load of 19 Watts where the pPVC is assumed to completely decompose.

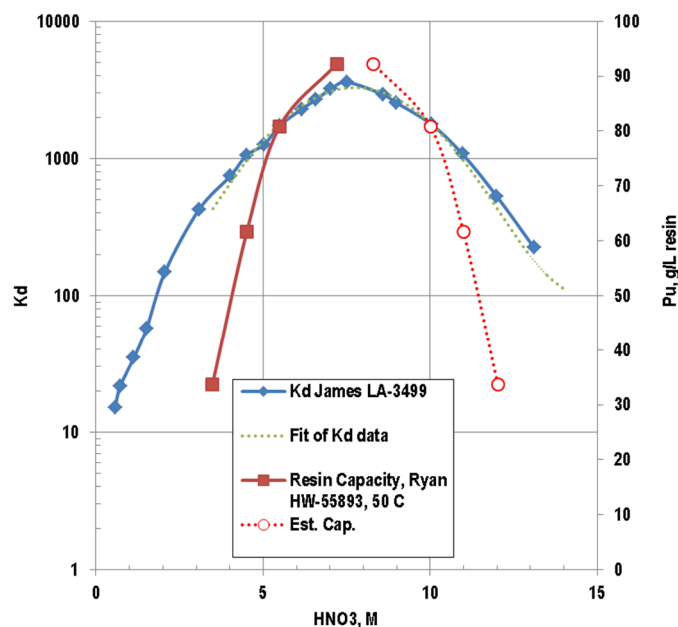
Contributors to the pressurization of the 9975 shipping package include radiolysis of adsorbed water on the plutonium dioxide, gas generation due to the decomposition of pPVC, helium gas generation (i.e. alpha particle emissions), and heating of the initial gas in the PCV.

Understanding the Range of Safe Wash Acid Concentration for Pu Anion Exchange Columns

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SRS's HB-Line facility receives Pu nitrate solution, purifies it by anion exchange and produces a Pu oxide product after oxalate precipitation followed by calcination. Historically this process operated in a narrow operating band with established process limits for the loading and washing steps of 6 to 9 M nitric acid concentration. Due to increased rigor demanded on safety basis and criticality related limits, sampling and measurement uncertainty allowances have reduced the region of acceptable operating conditions and could call into question authorization basis compliance when sampling or analytical analyses were found to be invalid. As a result, SRNL was requested to evaluate the true safety limits for anion exchange loading and washing process steps. During the wash step, excessively high or low wash acid concentration has the potential to cause an unsafe condition because this solution is automatically transferred to large storage tanks. Unfavorable conditions for Pu retention on the resin could cause a partial elution of the column. SRS has historically observed a 9 M nitric acid upper acid limit for resin safety but did not acknowledge that the possibility of exceeding the safe Pu solution concentration if a loaded Pu column were washed with greater than 12 M nitric acid (due to the reduced resin capacity). Similarly at low nitric acid concentrations (between 1 and 6 M) the Pu concentration would exceed the safe Pu solution concentration. Figure 1 shows K_d and Pu resin loading capacity data from the literature illustrating the nature of the problem. Progress-to-date of this investigation will be presented.



Radiolytic degradation of solvent extraction ligands in the presence of metal ions*Randy Ngelale and Mikael Nilsson*

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Department of Chemical Engineering and Material Science

Due to the intense radiation of used nuclear fuel, solvent extraction processes designed to treat this material experience degradation of the extracting ligand. The products of the degradation can adversely affect the efficiency of the overall extraction process as well as form a third phase or lower the selectivity of the extraction. In the case of the PUREX process we study the effects of metal loading of tributyl phosphate (TBP) on the degradation caused by acid hydrolysis, low LET gamma radiolysis and high LET alpha radiolysis (using the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ reaction). The results discussed will be of our system of 0.1M TBP/dodecane contacted with 3M nitric acid and varying concentrations of uranyl nitrate to observe the effect of increased metal loading. Samples were analyzed by gas chromatography the change in concentration of total and free TBP (defined as the TBP not complexed by uranium uptake) to see if depositing a fixed dose over a short amount of time (indicative of high LET) or the same fixed dose over a prolonged period of time (indicative of low LET) have varying effects in the metal loaded organic phase.

Particulate Separation from the Outlet of Plutonium Pyrochemical Processes

David A. Parkinson, J. Matt Jackson, Sheldon K. Apgar, P. Michael Brooks, Christopher W. Thorn

Metal Chlorination and Direct Oxide Reduction processes performed in the Plutonium Processing Facility at TA-55 produce outlet gas streams contaminated with debris particles. These particles must be removed to protect equipment downstream. The goal of this project is to design, evaluate, and test a separator that removes particulates from the exhaust stream and minimizes the potential for flow blockage. Two basic separator designs were considered: a cyclone and an impingement separator. Several cyclone and impingement type designs were created in SolidWorks[®] software and tested using imbedded computational fluid dynamics (CFD) software Flow Simulation[™]. It was determined that a cyclone design would have to become increasingly small to perform effectively at the low volumetric flow-rates of the processes. With the high priority placed on minimizing flow restriction, it was determined that a cyclone of these dimensions would not be practical. The initial impingement separator showed good separation results. This design was optimized using the CFD software to obtain maximum efficiency. A prototype separator was fabricated, and laboratory testing will begin in the near future. Results from these tests will be presented at the time of the symposium.

Lab-scale Testing of a Codecontamination Process

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Argonne National Laboratory

To be presented at the 2016 Actinide Separations Conference

Codecontamination is a solvent extraction process that uses tributyl phosphate (TBP) to co-extract U, Pu, and Np from spent fuel dissolved in nitric acid, followed by selective stripping to recover U/Pu/Np in a single product stream and the remaining U in a second effluent. For successful separation, the process requires predictable control of the behavior of the key species involved in the separations. In terms of flowsheet design, the major factors include controlling the U:TRU ratio in the U/Pu/Np product, directing the majority of the Np to the U/Pu/Np product, minimizing the extraction of fission products (specifically Mo, Ru, and Zr), and controlling Tc behavior. To that end, lab-scale flowsheet testing has been divided into three components: (1) demonstrating that extraction of the key fission products, Ru, Mo and Zr is controlled as predicted by the Argonne Model for Universal Solvent Extraction (AMUSE) code, (2) characterizing the extraction of Np as a function of redox chemistry, and (3) demonstrating the partial stripping of U in the second segment of the process. The first and third components require testing the full flowsheet, while the second component is being studied using microfluidics and single-stage tests. Multistage tests were run with a lab-scale 2-cm contactor to validate the design criteria used to develop the flowsheet. Tests of the first and second segment of the Codecontamination flowsheet are described. A number of small-scale tests using a microfluidic system were run to bracket the stable operating regime for Np. By varying flow rates and capillary lengths, mass transfer and kinetics data can be elucidated for Np in the TBP/alkane-nitric acid system.

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Purification of ^{229}Th for measurement of nuclear isomeric transition at LANL

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Introduction

The ^{229}Th nucleus possesses the lowest-energy nuclear isomeric state known with potentially exciting applications in nuclear, atomic, condensed matter and optical physics, quantum information, metrology and cosmology. The direct measurement of the ^{229}Th nuclear isomeric transition energy has been very challenging due to the lack of a strong signal, slow data rate, and various background interferences. Despite the efforts of several groups around the world, which span three decades, the transition energy remains a mystery. Thorium-229 doping of appropriate crystals may enable the accurate measurement of the isomeric transition energy. This would clear the path for laser spectroscopy and quantum manipulation of the ^{229}Th nucleus, as well as the study of interactions of the $^{229\text{m}}\text{Th}$ atomic nucleus with host materials and the development of a ^{229}Th nuclear clock. In this work, we present a method for the purification of ^{229}Th solution from salt contamination in order to provide a pure source for crystal doping.

Materials and Methods

Recovery of thorium from an unknown solution (~500 mL) was performed via ion exchange chromatography. The solution was first evaporated to dryness and then re-dissolved in 8 M HNO_3 . This second solution was passed through a Bio-Rad Ag1x8 anion exchanger column, and thorium retention was achieved. Different dilution volumes and column sizes were tested to maximize retention of thorium with a minimal loading volume. Thorium was eluted, and the thorium fraction was analyzed via gamma-ray spectrometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the presence of radionuclidic and radiochemical impurities.

Results and discussions

After evaporation of the initial thorium solution, a white crystalline solid was present, which was assumed to be NaCl from previous experiments. Due to the high salt concentration, thorium could not be retained on the anion exchanger column in 8 M HNO_3 quantitatively. The thorium solution was thus processed in several portions. A ^{229}Th activity of 5.8 MBq (156.7 μCi) could be recovered, corresponding to 97% of the activity in the raw solution. ICP-AES analysis showed no other significant radiochemical impurities. Thorium mass is represented by ^{229}Th isotope that make this sample very convenient for small crystal doping. Recovered ^{229}Th was reprocessed on a small (1 mL) anion exchanger column. Expected sorption behavior in 8 M HNO_3 and the absence of residual salt particles was demonstrated in this second purification step.

Acknowledgments: This material is based upon work supported by the United States Department of Energy, [Laboratory Directed Research & Development \(LDRD\)](#) via an award from Directed Research Program at LANL

Determination of Pu Isotopic Abundances Using an Alpha Spectrum Peak Fitting Algorithm

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The poster will describe the entire process - from the sample preparation to spectrum peak fitting algorithm - for measurement of separate ^{239}Pu and ^{240}Pu activities using silicon detector based alpha spectroscopy. The typical commercially available alpha spectroscopy system is capable of measuring distinct ^{242}Pu and ^{238}Pu activities but not distinct separate activities for ^{239}Pu or ^{240}Pu . These two major isotopes of plutonium have alpha particle energies within a range of 65 keV - in comparison to the energy resolution of a typical silicon detector being about 20 keV. Therefore, the alpha spectral peaks for ^{239}Pu and ^{240}Pu show significant overlap and appear as a highly-convoluted multiplet when using a typical silicon detector. The only way to make separate ^{239}Pu and ^{240}Pu activity measurements using silicon detector based alpha spectroscopy is to use a peak fitting routine to mathematically deconvolute and quantify the individual contributing peaks. Samples were first purified using column chromatography with Lewatit MP 5080 resin (60-150 mesh size) and then electrodeposited onto a stainless steel substrate for alpha spectroscopy. The sample preparation steps are important to achieve the best possible spectral resolution. It is also important to completely remove ^{241}Am from the sample as its alpha particle energies interfere with ^{238}Pu alpha particle energies. The peak fitting routine that is used in this work utilizes the determined ^{238}Pu peak fitting parameters to assist in the deconvolution of the associated overlapping ^{239}Pu and ^{240}Pu peaks. This entire process was tested using U.S. DOE New Brunswick Laboratory (NBL) Pu CRMs and actual Pu samples including plutonium-beryllium (PuBe) alloy samples. The Pu isotopic data from this sample set will be compared to data from Thermal Ionization Mass Spectrometry (TIMS) determinations - the well accepted standard for Pu isotopic abundance measurements.

This document had been reviewed and assigned publication number: 'LA-UR-16-22924'.

Ion-Exchange Based Separation of Americium

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Studies at the Savannah River National Laboratory have examined whether minor actinide separations can be accomplished effectively using inorganic-based ion-exchange materials through the strategic use of the oxidizing agent, sodium peroxydisulfate, to oxidize Am(III) to Am(V) in dilute acidic solutions. Current work is investigating a flowsheet concept where ion-exchange of Am(III) and fission products (Lanthanides, Cs, Sr, Tc) is followed by recovery of the Am using an oxidizing eluent. This flowsheet concept would use a conventional ion-exchange column and resin that exhibits high affinity for more highly charged ions such as the lanthanides (Ln(III)) and +3 actinides (Am, Cm) and +4 metals (Zr, Pu). The ion-exchange resin has a reduced affinity for sorbates that have low charge density (e.g., actinyl ions, Cs^+ , Sr^{2+} and TcO_4^-). The actinyls, Cs^+ , Sr^{2+} and TcO_4^- would pass through the column and be collected for further processing or disposed of as waste. The Am(III), Cm(III), Ln(III), Pu(IV) and Zr(IV) would be retained on the resin. Am(III) would be selectively recovered by eluting with a oxidizing eluent. After removal of the Am, the Cm(III), Ln(III), Pu(IV), and Zr(IV) would be eluted with 0.1 M nitric acid and disposed of as waste. Depending on the oxidizing reagent used, oxidation of Pu(IV) to the PuO_2^+ or PuO_2^{2+} will likely occur and be stripped along with the americium. The oxidation of Am(III) sorbed onto the resin will likely require an elevated temperature (e.g., 80 – 95 °C) that could impact the resin loading and chemical stability.

Ion-exchange tests were performed using three materials, (1) monosodium titanate (MST), (2) the commercially available sodium nonatitanate (SrTreatTM), and (3) an unconventional metal organic framework material prepared by Texas A&M University researchers. Oxidizing agents tested include ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and ozone. The ion-exchange oxidative strip tests were performed in dilute nitric acid solutions (pH 1 – 4).

We acknowledge the US Department of Energy, Office of Nuclear Energy, Materials Recovery and Wasteforms Development Campaign for funding this work.

Infrastructure Improvement for Analytical Chemistry and Materials Characterization Capabilities at Los Alamos National Laboratory

Amy S Wong, Denise Thronas, Tim Nelson, and Louis Schulte
Chemistry Division and Plutonium Strategy Infrastructure Division
Los Alamos National Laboratory

The Science of Signatures (SoS) is one of four science pillars championed by the Laboratory. Analytical chemistry (AC) and materials characterization (MC) capabilities provide critical measurements and characterizations in the areas of nuclear/radiological, chemical and materials signatures. These capabilities support national security missions by providing a safe, secure, and effective nuclear stockpile, as well as providing important attributes of interdicted materials for protecting against nuclear threats. The current AC labs in the Chemistry and Metallurgy Research (CMR) facility was designed and constructed more than 64 years ago. The majority of MC capabilities are also in a less than optimal configuration in Plutonium Facility-4 (PF-4).

In June 2013, the Chemistry and Metallurgy Research Replacement (CMRR) Project completed the first phase of plutonium infrastructure improvement by outfitting half of the lab space in the Radiological Laboratory/Utility/Office Building (RLUOB) with modern and state of the art analytical equipment. Subsequently, in August 2014, the CMRR Project started new phases of equipment installation by relocating the remaining AC and MC capabilities from the CMR facility to RLUOB and consolidating in the improved lab space in PF-4. This project represents an unprecedented, multi-billion dollar investment in plutonium infrastructure improvement and chemical/materials science capabilities by the National Nuclear Security Administration (NNSA). The CMRR Project includes the design, procurement, construction, start-up, and transfer of AC/MC capabilities from CMR to TA-55, allowing Laboratory to continue its mission to maintain and certify the U.S. nuclear stockpile, be a leader in the SoS strategy, and sustain its status as the Plutonium Center of Excellence.

Characterization of *f*-element oxide stoichiometry and phases through Raman Spectroscopy

Jared T Stritzinger, George S. Goff, and Dave M. Wayne

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The fluorite structure is well represented in the lanthanide and actinide series by the MO₂ oxides of Ce, Pr, Tb, Th, U, Np, Pu, Am, Cm and Cf. These oxides are often thought of as stoichiometric; however, MO_{2±x} often is a better reflection the true non-stoichiometric nature of these oxides. The robustness of the fluorite structure type easily accommodates oxygen loss or gain, while preserving the over-all metal cation lattice. This is often observed only as an expansion of the unit cell for the MO₂ in Powder X-ray Diffraction (PXRD) but rarely provides insight to the oxygen sublattice. Raman spectroscopy is sensitive to shifts in the coordination environments as symmetry is broken and new vibrational modes are allowed. The stoichiometric fluorite structure type shows O_h⁵ symmetry with one Raman active mode arising from the T_{2g}. Examination of sub-stoichiometric Praseodymium oxides and a variety of Uranium Oxides shows the effect of oxygen stoichiometry on the fluorite structure and the resulting Raman spectroscopy. This allows for multiple phases to be distinguished with Raman Spectroscopy in samples where bulk characterization such as PXRD shows one phase

Hydrogen Generation in Aqueous Tanks at the LANL Plutonium Facility

Mary Ann Stroud and Casey Finstad

Los Alamos National Laboratory

LA-UR-16-22661

In TA-55, PF-4 aqueous operations, hydrogen (H₂) accumulates in process and storage tanks due to alpha particle radiolysis in solutions containing Pu and Am. Tank purging is required to maintain the amount of H₂ below an approved level. Previously, aqueous tanks were purged when the H₂ concentration was calculated to reach 90% of the lower flammability limit (LFL).

The criteria to determine when a tank will be purged have been modified. The tanks are purged before both of the following criteria are calculated to be met:

- the concentration of H₂ in tank headspace is calculated to reach a given value, currently the LFL, 4 mol% [volume], and
- the total moles of H₂ is calculated to reach a given maximum allowed value, currently 0.2 moles.

New calculations estimate the required date a tank needs to be purged based on the modified criteria. The new calculations also account for reduction in hydrogen concentration in the tank due to advection as well as diffusion. These calculations, as well as hydrogen generation results in processing tanks under typical processing conditions, will be discussed.

Silica-Salophen Hybrid Material for Uranium Sequestration

Jaclynn Unangst - Department of Chemical Engineering and Materials Science, Ken Shea - Department of Chemistry, Mikael Nilsson - Department of Chemical Engineering and Materials Science, University of California, Irvine

Selective uranium ion complexation is an active area of research that has potential in nuclear fuel sourcing, remediation, containment and sensing. In this current research Schiff Base chemistry is the foundation for a nonsymmetrical salophen synthesized in a multistep approach for incorporation into a silica-based hybrid material for uranyl ion, $[\text{UO}_2]^{2+}$ sequestration. The salophen ligand utilizes a (propyl)triethoxysilyl tether for covalent attachment into the hybrid material formed through co-condensation reactions of Stöber silica and the bridged polysilsesquioxane (BPS), bis(trimethoxysilyl)ethyl benzene. The hybrid material is chosen based on the robustness of silica with enhanced porosity from the bridged polysilsesquioxane. Previous studies using salophen have shown that it can complex uranium in solution. It is the goal of this research to find the optimal balance of salophen ligand, silica and BPS concentrations to give desirable surface area, functionalization and porosity for maximum uptake of the uranyl ion from aqueous environments. Uptake testing will show the efficiency and selectivity of the hybrid material at sequestering uranium.

Mitigation of Chloride Contamination in the Plutonium Feed Stream for Aqueous Nitrate Processing

Yvonne Martinez, Crestina Vigil
Los Alamos National Laboratory

Los Alamos National Laboratory safely and efficiently processes actinide materials to fulfill programmatic needs. Ion exchange effluents and precipitation filtrates are processed using an evaporator system for recovery and reuse of nitric acid as well as volume reduction of waste.

Even low concentrations of free chloride ions, perhaps as low as a few hundred parts per million, in the nitric acid process solutions can contribute to corrosion in the stainless steel evaporator leading to premature equipment failure. For this reason, plans have been developed for (1) inline analysis of chloride within the PF-4 plutonium processing facility at LANL and (2) elimination of the chloride, including a water or dilute acid wash of the plutonium oxide feed, stripping of the chloride during dissolution in nitric acid, or disposal of the chloride containing ion exchange effluents without evaporation or recycle. Plans for implementation of these techniques into the LANL processing facility will be discussed.

Quantifying TBP dimers and trimers in alkane solutions via Simulations and Experiments

Quynh N. Vo, Jaclynn L. Unangst, Liem X. Dang, Hung D. Nguyen, Mikael Nilsson

Tri-n-butyl phosphate (TBP), a representative of neutral organophosphorous ligands, is an important extractant used in solvent extraction process for the recovery of uranium and plutonium from spent nuclear fuel. This study utilizes molecular dynamics (MD) simulations in conjunction with experimental work to elucidate the self association of TBP in alkane solutions. Microscopic pictures of TBP isomerism and its behavior in n-dodecane diluent were investigated utilizing MD simulations. 2D potential mean force calculations were performed to characterize the conformational criteria for TBP dimers and trimers. For validating our simulations we investigated the self-association behavior of TBPs in various alkane diluents of different chain lengths (8, 12 and 16 carbons) and a branched alkane (iso-octane) by Fourier Transform Infrared Spectroscopic (FTIR) measurements. Our results indicate that TBP does not only self-associate to form dimers, as previous studies showed, but also trimers in the practical concentration range. Using a mathematical fitting procedure, the dimerization and trimerization constants were determined. As expected, these equilibrium constants are dependent on the solvent used. As the alkane chain for linear hydrocarbon solvents becomes longer, dimerization decreases whereas trimerization increases. For the more branched hydrocarbon, we observe a significantly higher dimerization constant. These effects are most likely due the inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain as all solvents in this study are relatively non-polar.

We found that the dimerization and trimerization constants of TBP in n-dodecane determined by MD simulations compared favorably with our FTIR study. These results further confirm the accuracy of our theoretical models for TBP and n-dodecane molecules. The new insights into the conformational behaviors of TBP molecule as a monomer and as part of an aggregate could greatly aid the understanding of the complexation between TBP and metal ions in solvent extraction system.

May 25, 2016 (Wednesday -Morning)
Session 2: Sigma Team for Minor Actinide Separations
Session Chair: Mark Jensen, Colorado School of Mines

8:00 AM	Announcements	
8:05 AM	Heavy actinide-dipicolinic acid complexation thermodynamics	Jenifer Braley – Colorado School of Mines
8:30 AM	Catalytic Oxidation of Americium in Nitric Acid Solutions	George Goff - LANL
8:55 AM	Characterization of Diethylenetriamine-N,N'-di(acetylglycine)-N,N',N''-triacetic acid (DTTA-DG) as a Ligand for Enhanced Americium(III) Differentiation	Colt Heathmann – INL
9:20 AM	Supramolecular separation of the actinides Using Biomolecules	Mark Jensen – Colorado School of Mines
9:45 AM	Morning Break	BREAK
10:05 AM	Synthesis and Evaluation of Novel Rigid 1,10-Phenanthroline Bis lactam Ligands for Am(III) Separation over Eu(III) from Highly Acidic Solution	Santa Jansone-Popova - ORNL
10:30 AM	Achieving Hexavalent Actinide Separations using Copper (III) Periodate	Kevin McCann – Colorado School of Mines
10:55 AM	Hexavalent Am for Separations: Toward Actinide Co-extraction for the fuel cycle	Bruce Mincher – INL
11:20 AM	Solvent Extraction of Electrochemically Generated Am(VI) using DAAP	Christopher Dares – UNC @ Chapel Hill
11:45 AM	Accomplishing Equilibrium in ALSEP: Demonstrations of Modified Process Chemistry on 3-D Printed Enhanced Annular Centrifugal Contactors	Artem Gelis – ANL
12:10 PM	Afternoon Open for Discussions	

Heavy actinide-dipicolinic acid complexation thermodynamics

Jenifer C. Braley

Colorado School of Mines

Research using (poly)aminopolycarboxylate (APC) ligands to accomplish trivalent actinide / lanthanide separation has expanded significantly due to the development of derivative TALSPEAK solvent extraction processes that either simplify organic phase speciation (i.e. TALSQueak)^[1] or streamline processing steps through combining neutral and organic phase extractants (i.e. TRUSPEAK or ALSEP).^[2,3] Courtesy their applications in over fifty years of actinide separation science, the best defined interactions of actinides with soft donors in aqueous solutions involve APC ligands. The thermodynamics of these interactions are usually defined in terms of stability constants, especially for the trans-ameridium actinides, with minimal dialogue regarding enthalpic and entropic contributions to the binding. Compiling complete thermodynamic information (ΔH and ΔS , as well as ΔG) for the transplutonium actinides may be helpful in unraveling certain chemistries of the heaviest actinides (Bk-Fm). Recent reports with soft ligands, borate and dipicolinic acid, suggest significantly different chemistry presents for californium relative to the lighter (Pu-Bk) actinides.^[4,5] Preliminary complexation thermodynamics assessed in this work for actinides-dipicolinates, show californium dipicolinate complexes are slightly weaker than the berkelium dipicolinate complexes. The enthalpies for the californium dipicolinates are also significantly less exothermic than the berkelium dipicolinates. While somewhat preliminary, this data, and other data compiled in the literature, suggests near-degeneracy (e.g. ‘weak’) covalent interactions, as opposed to the more classically considered orbital overlap covalency, may be a unique feature of californium chemistry relative to earlier actinides.

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Catalytic Oxidation of Americium in Nitric Acid Solutions

George S. Goff, Lani Seaman, Kevin Boland, Laura Wolfsberg, and Wolfgang Runde

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Americium (Am) is one of the highest contributors to thermal loading and radiotoxicity of used nuclear fuel (UNF) due to the long half-lives of its primary isotopes and the decay of ^{241}Am to the long-lived ^{237}Np daughter isotope. The separation and transmutation of Am (with or without Cm) is under development within the DOE FCR&D program. Various research efforts have shown the viability of oxidizing americium to higher oxidation states (particularly +V, and +VI) under conditions where the lanthanides remain in the +III oxidation state. Stabilizing Am in these oxidation states could allow for selective separation of Am from the other trivalent f-elements and could easily be integrated with conventional PUREX or UREX-based flowsheets. Several extraction systems are being developed within the Sigma Team for separations from nitric acid solutions, yet oxidizing and holding Am in the higher oxidation states remains challenging in acidic solutions. We will present recent results on our experiments exploring the catalyzed ozone oxidation of Am(III) to Am(VI) using silver and cobalt as homogeneous catalysts, as well as the stability of Am(VI) in the presence of these catalysts.

Characterization of Diethylenetriamine-*N,N'*-di(acetylglycine)-*N,N',N''*-triacetic acid (DTTA-DG) as a Ligand for Enhanced Americium(III) Differentiation

Colt R. Heathman, Travis S. Grimes, Peter R. Zalupski

Idaho National Laboratory

Deployment of an advanced nuclear fuel cycle (after 60+ years of R&D activities) requires the development of an industrial partitioning scheme to separate Am from PUREX raffinate. Isolation of Am reduces the thermal heating and radiotoxicity of used fuel. One option to manage Am after its separation is transmutation in Generation IV reactors or accelerator-driven systems. The efficient differentiation of Am from the lanthanides is crucial to this option due to the greater lanthanide neutron capture affinities. Separation of trivalent actinides from trivalent lanthanides, challenged by similarities in ionic radii and charge density, has been accomplished using reagents containing soft donor groups. One commonly used class of N-donor compounds is the family of aminopolycarboxylate complexants (APC), such as ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA). Only a select number of APC's possess the unique aptitude to afford efficient An/Ln differentiation. Over the past half century fundamental building blocks necessary to support *f*-element group differentiation have been identified. Diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid (DTPA) (a member of the APC family) has been extensively studied, in conjunction with bis(2-ethylhexyl)phosphoric acid (HDEHP). However in centrifugal contactor equipment the viability of using DTPA is limited by metal exchange kinetics. The polydentate nature of DTPA results in strong thermodynamically stable complex, thus metal-complex dissociation requires significant reorganizational energy to allow for metal release.

This work aims to develop structure-function relationships to identify necessary building blocks to enhance the dissociation of metal ligand complexes. There are two options to increase metal exchange rates: (1) direct modification of the coordination pocket, and (2) functionalization of APC reagents to afford An/Ln separation in regions of higher acidity to promote dissociation of complexes. In a recent publication^[1] we reported the successful partitioning of Am from Ln's with bis-amide functionalized EDTA to fine-tune the metal binding structure and observed a significant reduction in the \sum pKa's, with minimal impact on metal coordination. This work evaluates the kinetic, coordination behavior, and thermodynamic features of diethylenetriamine-*N,N'*-di(acetylglycine)-*N,N',N''*-triacetic acid (DTTA-DG) (a bis-amide functionalized DTPA) to differentiate americium(III) from lanthanides to improve on the kinetic limitations of DTPA.

- 1) C.R. Heathman, T.S. Grimes, P.R. Zalupski, Thermodynamic and Spectroscopic Studies of Trivalent *f*-element Complexation with Ethylenediamine-*N,N'*-di(acetylglycine)-*N,N',N''*-diacetic acid. *Inorg. Chem.* **2016**, 55, 6, 2977-2985.

Supramolecular separations of the actinides Using Biomolecules

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The design of separations agents for metal ions in aqueous media has traditionally focused on the thermodynamics and kinetics of the metal-ligand bond. While this metal-centered approach works for separating many metal ions, some biological systems that naturally bind, sense, and transport transition metals with high specificity offer alternative approaches to separating metal ions from aqueous solutions. To control the trafficking of natural metal ions in living systems, networks of small molecules, peptides, and proteins work together in multiple steps and at a multiple of length scales to deliver the correct metals to the correct locations at the proper time. We are interested in co-opting this natural chemistry to separate synthetic elements, like the radioactive transuranium actinides, in new ways using supramolecular interactions.

Our work has focused on exploiting the supramolecular chemistry of the iron transport protein transferrin to separate actinide elements (e.g. plutonium) based on supramolecular protein-protein interactions that are governed by the overall conformation of the metal-transferrin complex. Transferrin possesses two specific metal-binding sites with identical ligand groups that bind tetravalent actinides strongly; however the protein responds differently to plutonium depending on which of the binding sites contain plutonium. We have used X-ray absorption, small angle X-ray scattering, NMR, isotopic labeling, and kinetic studies to understand the features of plutonium chemistry that control the conformation of plutonium-transferrins and the resulting supramolecular interactions between proteins. Our results suggest that the size and coordination preferences of the tetravalent actinides and their interactions with non-protein ligands drive the conformational changes essential to the supramolecular recognition and subsequent separation of actinide transferrins.

Synthesis and Evaluation of Novel Rigid 1,10-Phenanthroline Bislactam Ligands for Am(III) Separation over Eu(III) from Highly Acidic Solution

Santa Jansone-Popova, Vyacheslav Bryantsev, Frederick V. Sloop, Radu Custelcean, Madeline Dekarske, and Bruce A. Moyer

Oak Ridge National Laboratory

The removal of minor actinides (MA) is of great importance for the safe disposal, storage, and recycling of spent nuclear fuel. Particularly challenging is removal of americium, which is a strong heat emitter, from the radioactive waste. Achieving substantial reduction of Am levels in the spent fuel would minimize the heat load and radiotoxicity of geologic repositories. In particular, selective separation of MA from other fission products, especially the lanthanides, is a daunting challenge owing to the fact that MA(III) and Ln(III) have similar chemical properties: oxidation state, ionic radius, hydration, and complexation behavior. Ligands with soft nitrogen donor atoms have been identified as selective MA(III) extractants. However, structurally similar tetradentate ligands based on the phenanthroline scaffold with combination of nitrogen- and oxygen-based binding sites, such as **1**, have been proposed as an alternative to nitrogen based ligands. Recent theoretical reports suggested that mixed *O,N*-donor ligands should exhibit improved selectivity towards An(III) over Ln(III).¹ Therefore, novel approaches towards the design and synthesis of mixed donor ligands capable of addressing these issues and realize their full potential in An(III) separation are highly desirable. We anticipate that the preorganization of the amide moieties in mixed-donor ligands will lead to markedly improved extraction performance in Am/Eu separation compared to their less rigid counterparts. Synthesis of these novel fused bislactam 1,10-phenanthroline ligands **2** and **3**, their solid-state complexes with lanthanides, stability and extraction studies will be presented.

We have prepared a new class of highly preorganized mixed-donor ligands for selective and efficient separation of Am(III) over Eu(III) from high nitric acid solutions. Practical synthetic approach utilizing powerful oxidative C-H functionalization reaction was used to construct unprecedented 1,10-phenanthroline bislactam motifs. Five isostructural 1:1 complexes of Ln(NO₃)₃ with novel norbornene derived 1,10-phenanthroline bislactam ligand **2** were synthesized and structurally characterized. Introduction of preorganization in the ligand structure through lactam formation (**2** and **3**) increases the Am(III) extraction efficiency by approximately 6 orders of magnitude compared to that of an acyclic 1,10-phenanthroline bisamide ligand **1**.

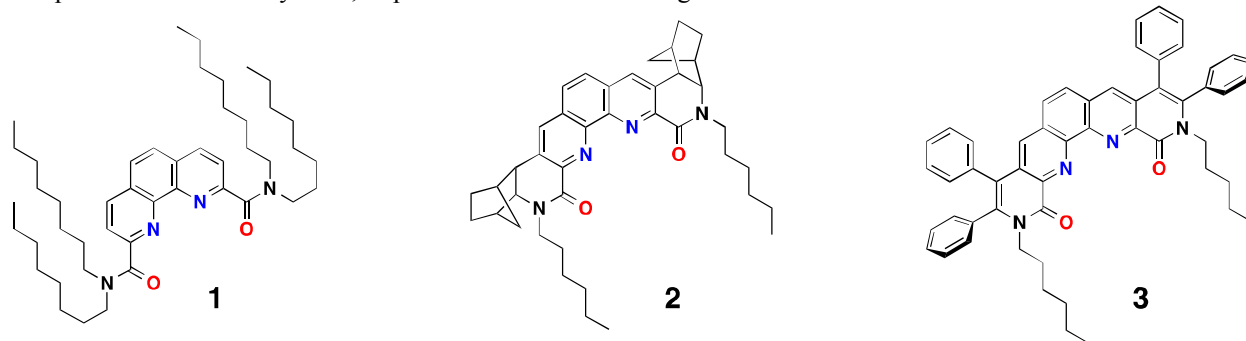


Figure 1. Chemical structures of novel preorganized bislactam ligands **2** and **3** and bisamide ligand – tetraoctyl-1,10-phenanthroline-2,9-dicarboxamide **1**.

- 1) Bryantsev, V.S.; Hay, B.P. Theoretical prediction of Am(III)/Eu(III) selectivity to aid the design of actinide-lanthanide separation agents. *Dalton Trans.* **2015**, 44, 7935-7942.

Achieving Hexavalent Actinide Separations using Copper (III) Periodate

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Separation of americium from curium is one of the most difficult elemental separations steps in closing the nuclear fuel cycle. One method under consideration to achieve americium/curium separations is to oxidize americium to the hexavalent state, forming a linear dioxo cation, while curium remains as a trivalent element. Forcing americium to the hexavalent state provides a possibility of achieving group actinide (U-Am) separation from Cm and the remaining fission products. Thus far, only sodium bismuthate has demonstrated the ability to oxidize and maintain Am in the hexavalent state in molar nitric acid for recovery using solvent extraction. Several different separation schemes have been considered using sodium bismuthate to recover Am, but the insolubility of NaBiO₃ in aqueous or organic phases could be a limitation in further process development. The work presented is a collaboration of solvent extraction studies performed at Colorado School of Mines (CSM) and Pacific Northwest National Laboratory (PNNL). Using tracer amounts of ²⁴¹Am a distribution value of 2 was achieved when Am was oxidized by Cu³⁺ periodate in molar nitric acid and extracted into diamyl amylphosphonate. The oxidation time was found to have no effect on distribution values, but the values were suppressed when aqueous/organic contact times were extended. Furthermore, separation of ²⁴¹Am from ²⁴⁴Cm was found to be viable using Cu³⁺ periodate as an oxidant.

Envisioning a hexavalent group actinide separation scheme, oxidation of ²³⁷Np and ²³⁹Pu using Cu³⁺ periodate was studied using UV-Vis-NIR spectroscopy at PNNL. After demonstrating the production NpO₂²⁺, PuO₂²⁺, and AmO₂²⁺ by Cu³⁺ periodate, the redox chemistry of extracted hexavalent actinides in the aqueous and organic phases was monitored using UV-Vis-NIR. While Am displayed trivalent, pentavalent, and hexavalent oxidation states during the separation process, Np(VI) and Pu(VI) were found to be stable throughout the separation. Additionally, distribution values can be assessed by monitoring the concentration of each species in the aqueous and organic phases. Work at CSM concluded that a short, 5 second contact time provided the highest distribution values for Am. Spectroscopic studies at PNNL found separation of Np and Pu reached equilibrium after only a 10 second contact time. This presentation will cover preliminary results that move nuclear fuel separations closer to a hexavalent group actinide process.

Hexavalent Am for Separations: Toward Actinide Co-extraction for the fuel cycle

Bruce J. Mincher

Idaho National Laboratory

The ability to co-extract U, Np, Pu and Am in a single step would greatly simplify the currently-envisioned advanced nuclear fuel cycle. Oxidation of Am to hexavalency is an option to achieve such a separation since any oxidant that will prepare AmO_2^{2+} , will also oxidize Np and Pu to their corresponding actinyl ions. As we have often reported, hexavalent Am can be prepared using sodium bismuthate in highly acidic solution in yields sufficient to allow successful partitioning from the bulk of lanthanides using 1 M diamylamylphosphonate (DAAP)/dodecane extraction. We have now extended this work to examine the alternative oxidant copper(III) periodate, and to the ligands diethylhexylbutyramide (DEHBA), and diethylhexylisobutyramide (DEHiBA).

The 1 M DEHBA/dodecane provides D_{Am} greater than or equal to those obtained when using DAAP as the extractant for bismuthate-oxidized solution. However, for copper(III) periodate, marginal results were achieved that indicate only partial oxidation. We attribute the superior performance of bismuthate to its ability to act as its own holding oxidant, due to continual dissolution of the solid-phase NaBiO_3 . Data showing the utility of bismuthate to oxidize Am in the presence of known reducing agents is provided. In contrast, Cu(III) is immediately soluble, and the color change associated with the reduction of the copper upon organic contact is visible and instant. This suggests that a holding oxidant will be required in tandem with homogeneous oxidative treatments.

Solvent Extraction of Electrochemically Generated Am(VI) using DAAP

Christopher J. Dares,^{a,b} Bruce J. Mincher,^c Thomas J. Meyer^a

^aThe University of North Carolina at Chapel Hill, ^bFlorida International University, ^cIdaho National Laboratory

We recently developed metal oxide electrodes surface derivatized with a terpyridine ligand capable of binding americium. Using these electrodes, we have successfully demonstrated the electrochemical oxidation of Am(III) to Am(VI) in 0.1 M nitric acid. This is of great interest in fuel recycle schemes to partition americium, which is a major heat contributor in nuclear waste. In the hexavalent oxidation state, americium features altered reactivity enabling a more facile removal from the trivalent minor actinides and lanthanides still present in the waste. Continuing our work in this area, we have begun to perform solvent extraction experiments with electrochemically generated Am(VI), using diamylamylphosphonate in dodecane. We will discuss our results, and some key findings which improve extraction efficiency.

Artem V. Gelis^a, M. Alex Brown^a, Kent E. Wardle^a and Gregg Lumetta^b

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Accomplishing Equilibrium in ALSEP: Demonstrations of Modified Process Chemistry on 3-D Printed Enhanced Annular Centrifugal Contactors

The major components of the modified ALSEP process have been demonstrated on a modified 2-cm annular centrifugal contactor with an enhanced mixing zone using stable fission products and radiotracers. The results show that by decreasing the pH of the minor actinide stripping solution, using HEDTA instead of DTPA, and increasing contact time, the process is very effective in separating americium from the lanthanides and the fission products. Lanthanide and Actinide speciation and extraction kinetics will be discussed as well.

May 26, 2016 (Thursday – Morning)
Session 3: Sigma Team for Minor Actinide Separations
Session Chair: Gregg Lumetta, Pacific Northwest National Laboratory

8:00 AM	Announcements	
8:05 AM	The influence of nitric acid on solvent extraction behavior of N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA) toward trivalent lanthanides in the ALSEP process	Emily Campbell - PNL
8:30 AM	Evaluation of the Aromatic Functionalized BTP 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine for Am/Eu Separation	Talon Hill - ORNL
8:55 AM	Aggregation and Synergism in Solvent Extraction	Andy Jackson – UC Irvine
9:20 AM	Current State of the Advanced TALSPEAK and ALSEP Systems for Actinide-Lanthanide Separations	Gregg Lumetta - PNL
9:45 AM	Morning Break	BREAK
10:05 AM	Molecular Dynamics Simulations and Experimental Studies of Tri-n-butyl Phosphate for Liquid-Liquid Extraction	Hung Nguyen – UC Irvine
10:30 AM	Examination of the impacts of gamma radiolysis upon the efficacy of an ALSEP process solvent	Dean Peterman - INL
10:55 AM	Network Analysis of Molecular Interaction in Molecular Dynamics Simulations of PUREX-type Systems	Michael Servis – Colorado School of Mines
11:20 AM	Separation ligand degradation by organic radical cations	Stephen Mezyk, Cal State Univ. Long Beach
11:45 AM	Impacts of structural variation of aminopolycarboxylate complexants on phase transfer kinetics and differentiation of trivalent actinides from trivalent lanthanides	Peter Zalupski – INL
12:10 PM	Lunch Break (until 1:30 PM)	

The influence of nitric acid on solvent extraction behavior of N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA) toward trivalent lanthanides in the ALSEP process

Emily L. Campbell¹, Tatiana G. Levitskaia¹, Kenneth L. Nash², Gregg J. Lumetta¹

¹Pacific Northwest National Laboratory

²Washington State University

The need for safe and cost effective disposal of used nuclear fuel (UNF) led to the development of the Actinide Lanthanide SEparation (ALSEP) concept. The ALSEP concept uses an organic solvent that combines the neutral diglycolamide extractant, N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA), and the acidic extractant 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester [HEH[EHP] to selectively extract lanthanides (Ln) and minor actinides (Am and Cm) from high level waste from TBP-based reprocessing operations. The minor actinides can then be stripped back into the aqueous phase using a buffered polyaminocarboxylic acid solution while trivalent Ln remain in the organic phase. ALSEP is advantageous in that it decreases the radiotoxicity of UNF by removing long-lived actinides from the waste stream, reduces the heat loading in a geological repository, and ultimately reduces the cost of separation.

Understanding the metal-ligand coordination of the extracted species is crucial to designing an improved and efficient extraction system, as well as for development of a thermodynamic model of metal extraction necessary for prediction of extraction under process applications. In order to understand the extraction mechanism of the ALSEP process, the neutral and acidic extractant must be investigated independently and systematically. This research focusses on the influence of nitric acid on the extraction behavior of T2EHDGA toward trivalent lanthanides.

Evaluation of the Aromatic Functionalized BTP 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine for Am/Eu Separation

Talon G. Hill,¹ Ai Lin Chin,² Serene Tai,² Jesse D. Carrick,² Dale D. Ensor,² Lætitia H. Delmau^{1*}

¹Oak Ridge National Laboratory

²Tennessee Technological University

Nitrogen based bis-triazinyl pyridine (BTP) ligands are effective to selectively extract Am(III) from nitric acid solutions containing light lanthanides. Typically planar aromatic functionalities result in poor solubility in polar diluents such as trifluoromethylphenyl sulfone (FS-13). An efficient solvation level of 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine (MethOxyBenzene-BTP, MOB-BTP) Shifted efforts toward evaluation of material in the separation of Am(III) from Eu(III). The performance of MOB-BTP was compared to that of a camphor substituted BTP (CA-BTP). The results of this investigation demonstrate the novel 3,3'-methoxy-BTP complexant dissolved in a polar diluent was a more efficient extractant for Am(III) at a lower concentration than CA-BTP under comparable conditions. General observations during this study conclude that a process solvent of MOB-BTP and FS-13 is not a feasible choice.

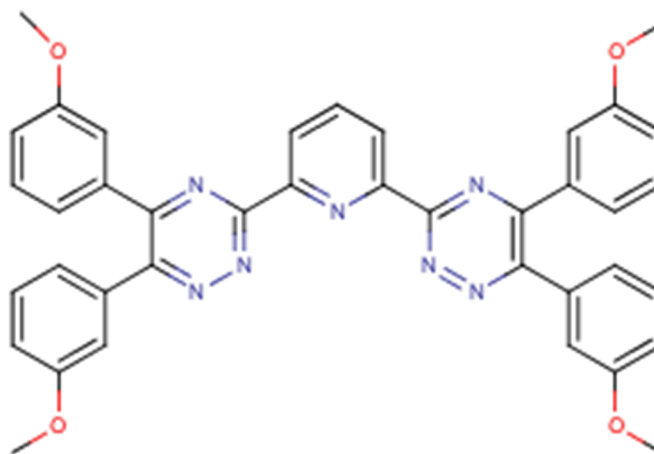


Figure 1. 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine

Aggregation and Synergism in Solvent Extraction

Andy Jackson, Mikael Nilsson

University of California Irvine

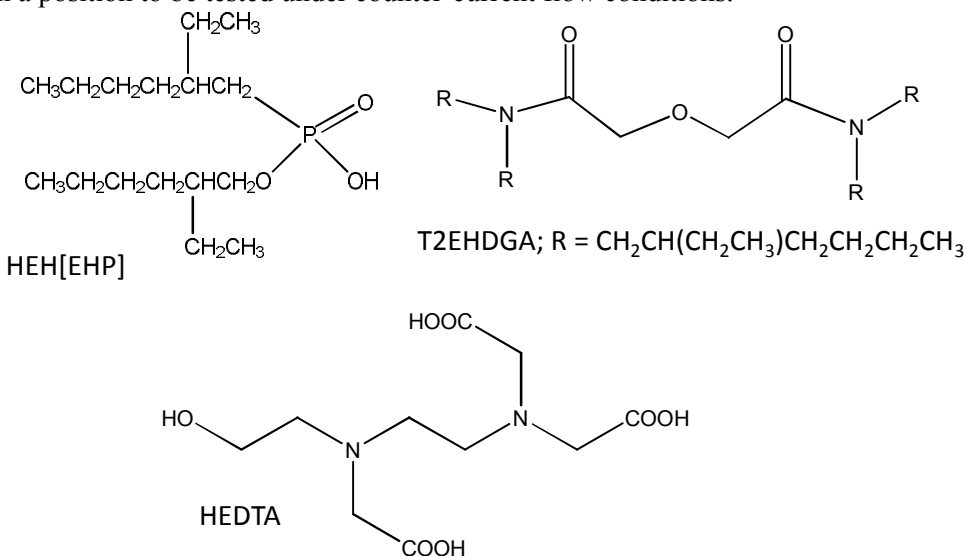
Partitioning of elements in used nuclear fuel is often accomplished through the use of solvent extraction. The proposition of extraction systems combining two extraction reagents is of recent interest as part of development of advanced fuel cycles. It is well known that the combination of reagents can, under certain conditions, interact and result in a significant increase in the extraction of the desired solutes a phenomenon known as synergism. It is also well known that many extraction reagents possess surface active properties which have been shown to lead to reverse micelle formation under the correct conditions. The presence of such aggregates has been suggested to catalyze the extraction of metal ions in some combined extractant systems.

This work examines the connection between synergistic extraction and the formation of aggregates in the organic phase of several known synergistic extraction reagent combinations. Properties of the organic phase are examined at equilibrium in an attempt to determine what aggregates may or may not be present. Several synergistic systems are first analyzed for synergistic behavior in metal extraction. Chosen were combinations of: 2-thenoyl trifluoroacetone (HTTA) and tributylphosphine oxide (TBPO), 2,2',6'2"-terpyridine (TERPY) and 2-bromodecanoic acid (BDA), and *N,N*-diisobutyl carbamoylmethylphosphine oxide (CMPO) and di-2-ethylhexyl phosphoric acid (HDEHP). Results indicate that while BDA:TERPY and HTTA:TBPO show synergism, organic phase water content is significantly different with HTTA:TBPO showing water uptake that matches the synergistic nature of the metal extraction at a much lower concentration than is seen in the BDA:TERPY system which also did not show the water uptake synergism. Synergistic metal extraction was not seen with the CMPO:HDEHP system.

Current State of the Advanced TALSPEAK and ALSEP Systems for Actinide-Lanthanide Separations

Gregg J. Lumetta, Amanda J. Casella, Gabriel B. Hall, Tatiana G. Levitskaia, and Sergey I. Sinkov
Pacific Northwest National Laboratory

Separation and transmutation *via* fissioning is one option being considered for managing the minor actinide elements (americium and curium) in the commercial nuclear fuel cycle. Our investigations into this topic has focused on solvent extraction based systems employing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) as the extractant. Two systems are considered. First, the Advanced TALSPEAK (trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes) concept involves selective extraction of the lanthanides into an organic phase containing HEH[EHP]; the actinides are held in the carboxylate-buffered aqueous phase by a polyaminocarboxalate ligand such as N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA).^[1] This approach requires an upstream process to first separate the lanthanides and actinides as a group. The second system we are investigating—the Actinide-Lanthanide Separation (ALSEP) concept—is designed to avoid this upstream processing step.^[2,3] In the latter case, the HEH[EHP] is mixed with N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA). The T2EHDGA serves to co-extract the actinides and lanthanides from molar concentrations of HNO₃ (i.e., directly from the raffinate of a tri-butyl phosphate based reprocessing flowsheet). The actinides are then separated from the lanthanides by selective stripping into a buffered polyaminocarboxylate solution. This paper will discuss recent progress made in resolving process chemistry issues associated with these two approaches, such that both systems are now in a position to be tested under counter-current flow conditions.



References

1. G.J. Lumetta, A.J. Casella, B.M. Rapko, T.G. Levitskaia, N.K. Pence, J.C. Carter, C.M. Niver, and M.R. Smoot, An Advanced TALSPEAK Concept Using 2-Ethylhexylphosphonic Acid Mono-2-ethylhexyl Ester as the Extractant, *Solvent Extr. Ion Exch.*, **2015**, 33, 211-223.
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- G.J. Lumetta, A.V. Gelis, J.C. Carter, C.M. Niver, and M.R. Smoot, The Actinide-Lanthanide Separation Process, *Solvent Extr. Ion Exch.*, **2014**, 32, 333-347

Molecular Dynamics Simulations and Experimental Studies of Tri-n-butyl Phosphate for Liquid-Liquid Extraction

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One of the most commonly used solvent extraction techniques is called PUREX (Plutonium URanium EXtraction), which employs tri-n-butyl phosphate (TBP) as an extracting agent to selectively complex. However, our understanding of the metal extraction mechanism and phase separation involve many molecular level events are far from complete. To gain insights into the thermodynamics and kinetics of interactions of TBP molecules with other molecules in extraction systems, both molecular dynamics (MD) simulations and experiments are performed.

In our simulation study, force field parameters for TBP have been determined by conducting a characterization study of TBP bulk liquid behavior using atomistic models with different sets of van der Waals and atomic charge parameters. Various properties of TBP in the liquid phase including the mass density, electric dipole moment, and self-diffusion coefficient are obtained and compared favorably with available experimental results [1]. Potential Mean Force calculations on a single TBP molecule show seven probable TBP isomers. Radial Distribution Functions of TBP suggests the existence of TBP trimers in n-dodecane diluent at high TBP concentrations in addition to dimers. Additional Potential Mean Force calculations performed to determine the angle and distance criteria for TBP dimers and trimers. The dimerization and trimerization constants of TBP in n-dodecane were obtained [2] and match our own experimental values using FTIR technique as described below [3]. The new insights into the conformational behaviors of TBP molecule as a monomer and as part of an aggregate could greatly aid the understanding of the complexation between TBP and metal ions in solvent extraction system.

In our experimental study, we first examined the self-association behavior of TBPs in various alkane diluents of different chain lengths (8, 12 and 16 carbons) and a branched alkane (iso-octane) by performing Fourier Transform Infrared Spectroscopic (FTIR) measurements [3]. Our results indicate that TBP does not only self-associate to form dimers, as previous studies showed, but also trimers in the practical concentration range. Using a mathematical fitting procedure, the dimerization and trimerization constants were determined. As expected, these equilibrium constants are dependent on the solvent used. As the alkane chain for linear hydrocarbon solvents becomes longer, dimerization decreases whereas trimerization increases. For the more branched hydrocarbon, we observe a significantly higher dimerization constant. These effects are most likely due the inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain as all solvents in this study are relatively non-polar.

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- 2) Quynh N Vo *et al.* Quantifying Dimer and Trimer Formation by Tri-n-butyl Phosphates in n-Dodecane: Molecular Dynamics Simulations, under review
- 3) Quynh N Vo *et al.* Quantifying Dimer and Trimer Formation of Tri-n-butyl Phosphates in hydrocarbon diluents: FTIR Study, under review.

Examination of the impacts of gamma radiolysis upon the efficacy of an ALSEP process solvent*Dean R. Peterman*

Idaho National Laboratory

The radiolysis/hydrolysis test loop, located at the Idaho National Laboratory (INL), was designed to allow the investigation of radiolytic and hydrolytic degradation processes which may impact the efficacy of a solvent extraction process flowsheet. Recently researchers at the INL have studied the impacts of gamma radiolysis on the Actinide Lanthanide Separation (ALSEP) extraction process. The ALSEP process was developed through a joint collaboration between Argonne National Laboratory and Pacific Northwest National Laboratory.¹ This process uses an organic solvent consisting of a neutral extractant, *N,N,N',N'*-tetra-2-ethylhexyl-diglycolamide (T2EHDGA) and an acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) dissolved in *n*-dodecane. The actinides and lanthanides are co-extracted from relatively high concentration nitric acid and the actinides are selectively stripped from the loaded organic phase using a carboxylic acid buffered polyaminocarboxylic acid solution.

To be applicable to the treatment of dissolved nuclear fuel on an industrial scale, a solvent extraction process must exhibit substantial resistance to radiolytic degradation. In order to evaluate the possible impacts of gamma radiolysis upon the efficacy of the ALSEP process, a series of experiments using air-sparged gamma irradiations and test loop irradiations have been performed. Two different ALSEP solvent formulations in contact with nitric acid were irradiated under static conditions. The impacts of gamma radiolysis were evaluated by measuring the variation in the values of D_{Am} , D_{Eu} , and D_{Ce} , determined using the irradiated ALSEP aqueous and organic phases, as a function of absorbed gamma dose. The results of the analyses performed on these irradiated phases were used to determine the ALSEP composition employed for the test loop irradiation experiments. The analysis of the test loop irradiation experiments will be presented and the potential impacts of gamma radiolysis upon the efficacy of the ALSEP flowsheet will be discussed.

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Network Analysis of Molecular Interaction in Molecular Dynamics Simulations of PUREX-type Systems

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Colorado School of Mines

Molecular association in organic phase systems related to PUREX-type extraction schemes are assessed with molecular dynamics simulation. Two types of simulation systems are presented. First, self-association of several organophosphorus solvating extractants, including tributyl phosphate (TBP) and diamyl amyl phosphonate (DAAP), is considered in a range of organic diluents. Second, extraction of water and nitric acid extraction by TBP is simulated in a dodecane medium. Experimental analysis of these systems is limited by ideality assumptions - simple speciation makes experimental assessment straightforward. When speciation becomes more complex (i.e. high concentrations of extractant or extracted nitric acid and water), the spectroscopic or scattering experimental approaches become limited in their utility to provide finer resolution of the underlying molecular interactions or structure. To analyze the more complex systems, molecular simulation can be employed, but traditional simulation analysis techniques, like snapshot visualization^[1] and radial distribution functions, are unable to provide a quantitative and precise picture of the complex speciation occurring in the considered systems.

Network analysis^[2] of extractant self-interaction and hydrogen bonding in the nitric acid and water systems, is therefore employed in simulations considered in this work to identify the exact speciation of the simulated systems. The dipole stacking that governs the energetics of aggregation for TBP and DAAP is affected by the number of molecules in a given aggregate. Dipole pairing, where the addition of an extractant molecule to an aggregate takes the aggregate from an odd number of constituents to an even number, is more favorable than the transitioning from even to odd. Furthermore, the extractant carbon tail length dictates the size of the aggregates up to which this phenomenon is observed. Questions have been raised through experimental study of the nitric acid and water extraction by TBP at high nitric acid concentrations concerning the topology of the extracted species^[3]. Simulation results, coupled with electronic structure vibration analysis calculations, are compared with experimental results. Simulations indicate a wide range of potential species formed from hydrogen bonding networks influenced by the presence of water.

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Separation ligand degradation by organic radical cations

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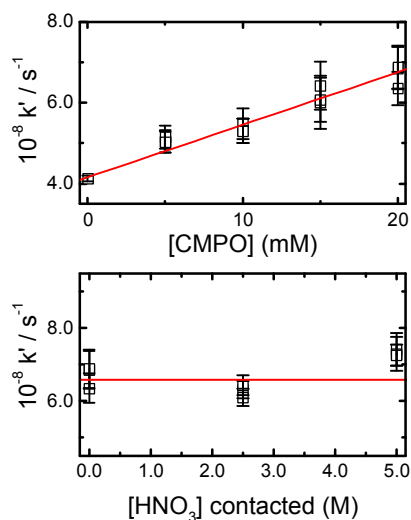
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The solvent-based extraction of used nuclear fuel uses designer ligands dissolved in an organic phase to extract ligand-complexed metal ions from an acidic aqueous phase. These extractions are anticipated to be performed in highly radioactive environments, and the radiation chemistry of these complexants and their diluents will be important in determining extraction efficiency, separation factors, and solvent-recycle longevity.

Although there has been considerable effort^[1-4] investigating ligand damage occurring in acidic water radiolysis conditions, only minimal fundamental kinetic and mechanistic data has been reported for the degradation of extraction ligands in the organic phase^[5]. The radiolysis of organic diluents (dodecane, TPH, kerosene) produces a mixture of radical cations ($R^{+\bullet}$), carbon-centred radicals (R^\bullet), solvated electrons (e^-_{solv}), and molecular products such as hydrogen (H_2). Typically, the radical species and electrons will react with the dissolved oxygen present to produce relatively inert peroxy radicals. The alkane radical cation species, $R^{+\bullet}$, is the major radiolytically-produced species that can react with, and degrade, extraction agents in this phase.

Recently, we have performed kinetic studies for organic radical cation reactions with various nitrogen-containing ligands (for example, CMPO). Fast kinetics were observed for dodecane radical cations, stressing the importance of this mechanistic pathway (see Figure 1). Minimal impact on acid-contact



was found for these kinetics. We are presently elucidating these parameters for a wide range of diluents and ligands, and combining them with the known acidic aqueous phase chemistry, will allow a full, fundamental, understanding of the impact of radiation on solvent extraction based separation processes to be achieved.

Figure 1. Top: Second-order rate constant plot for reaction of dodecane radical cation ($R^{+\bullet}$) with CMPO in dodecane/0.10 M CH_2Cl_2 at 295K.. Line is weighted linear fit, with slope of $k = (1.30 \pm 0.11) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, ($R^2 = 0.96$). Bottom: Measured rate constants for 20 mM CMPO in aerated dodecane/0.10 M CH_2Cl_2 contacted with different nitric acid concentrations showing no significant increase in reactivity.

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Impacts of structural variation of aminopolycarboxylate complexants on phase transfer kinetics and differentiation of trivalent actinides from trivalent lanthanides.

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It is difficult to rival the efficiency of separating trivalent lanthanides (Ln^{3+}) from trivalent actinides (An^{3+}) afforded by liquid-liquid distribution systems containing diethylenetriamine- $\text{N},\text{N},\text{N}',\text{N}',\text{N}''$ -pentaacetic acid (DTPA). This well-known aminopolycarboxylate complexant wraps around an actinide ion in aqueous mixture, while transfer of trivalent lanthanide ions into a non-aqueous environment is facilitated by a liquid cation exchanger. While the octadentate coordination of f -element by DTPA is largely responsible for the accomplished $\text{An}^{3+}/\text{Ln}^{3+}$ separation it is also liable for the slow liquid-liquid mass transfer. The binding pocket of such f -element / DTPA complex contains seven stable five-membered rings, with three nitrogens and five oxygens coordinating the metal ion. Due to the necessary structural reorganization of this polydentate reagent the complex dissociation suffers from kinetic limitations, and slows the attainment of the TALSEPAK-type liquid-liquid distribution equilibrium. This contribution will relate options for structural modification of aminopolycarboxylates, the corresponding disruption of f -element coordination sphere, and its effects on $\text{An}^{3+}/\text{Ln}^{3+}$ differentiation. Connections between thermodynamic studies on the trivalent f -element complexation by aminopolycarboxylates and phase transfer kinetic studies will be presented.

May 26, 2016 (Thursday - Afternoon)
Session 4: Separation Processing
Session Chair: Tracy Rudisill, Savannah River National Laboratory

1:30 PM	Announcements	
1:35 PM	Dissolution of irradiated MANTRA isotopic targets and preparation of ATLAS targets	Jeffrey Berg – INL
2:00 PM	Microfluidic and Millifluidic Separations for Actinide Processing and Analysis	Rebecca Chamberlin - LANL
2:25 PM	Small-Scale Tests in Support of Chemical Processes for Production of Pu 238	Laetitia Delmau – ORNL
2:50 PM	Structure and radiolytic stability of monoamide-actinide complexes	Philippe Guilbaud – CEA
3:15 PM	Afternoon Break	BREAK
3:35 PM	Calcium Reduction of Spent Electrowinning Salt	Clare Stawarz – AWE
4:00 PM	Historical Test Debris Analysis using Long Lived Lanthanides'	Veronika Mocko – LANL
4:25 PM	Alternative Chemical Cleaning Methods for High Level Waste Tanks	Tracy Rudisill – SRNL
4:50 PM	Break (until 6:30 PM)	BREAK

Dissolution of irradiated MANTRA isotopic targets and preparation of ATLAS targets

*Jeffrey F. Berg
Idaho National Laboratory*

The proper dissolution of samples is required for the presentation to an analytical instrument, in order to obtain reliable results. The irradiation of samples presents a new problem, in that the physical and chemical characteristic of the sample can greatly change. Analytical dissolution methods must recognize these changes, and be modified to deal with insoluble residue that may contain sample analytes of interest. This presentation will discuss the issues observed when dealing with irradiated sample dissolution, and the methods used to achieve proper sample dissolution.

The Analytical Laboratory received (67) irradiated MANTRA (Measurement of Actinide Neutronic Transformation Rates by Accelerator mass spectroscopy) samples for dissolution and analysis. These targets consisted of (7) stable fission product isotopes and (59) actinide isotopes, subjected to irradiation in the Advanced Test Reactor (ATR), located at the Idaho National Laboratory (INL). Additionally, there were (12) flux wire bundles in the experiment that consisted of cobalt, nickel, titanium, copper, iron, and uranium wires. The dissolved solutions were measured by Ion Coupled Plasma Mass Spectroscopy (ICP-MS) to determine analyte concentration, and Multi-Collector ICP-MS (MC-ICP-MS) to determine isotopic ratios. Thirty nine of the dissolved samples, consisting of eight target isotopes, were converted to oxide products for the preparation of samples for measurement by Argonne Tandem Linac Accelerator System (ATLAS), located at Argonne National Laboratory (ANL). This presentation will focus on the wet chemical methods used to dissolve the MANTRA target isotopes, flux wires, and methods to prepare the ATLAS samples.

The irradiated MANTRA isotopic targets (1-3 mg) were contained inside an aluminum capsule, and proved very difficult to dissolve. The validation methods performed on un-irradiated material were not successful. Methods were modified to achieve a complete dissolution. This presentation will discuss the problems observed dissolving these high fluence actinide samples and the possible causes for this difficulty. All samples were successfully dissolved with the refined method. The flux wire samples were dissolved using previous validation methods without difficulty. A brief discussion on the preparation of actinide oxide samples for ATLAS measurement is also included in the presentation.

Microfluidic and Millifluidic Separations for Actinide Processing and Analysis*Rebecca M. Chamberlin, Stephen L. Yarbrow, Ning Xu*

Los Alamos National Laboratory

Los Alamos has initiated a multi-disciplinary program in milli- and microfluidic actinide separations. These highly efficient separations at short length-scales have the potential to operate in a smaller footprint than conventional aqueous processing, allowing recovery of valuable floor space to support manufacturing goals. Additionally, higher efficiency processing may result in fewer residues to the vault and a lower volume of TRU waste. Plutonium process capabilities can be maintained and advanced through microscale implementation in low-hazard facilities, then numbered-up to high-throughput systems when national needs require increased material production rates. Measurement of mass transfer rates in well-defined microfluidic channels also allows rapid exploration of new solvent systems.

Analytical chemistry and bulk nuclear forensics have similar chemical separation needs, and microfluidic approaches can enable significant sample size reduction and automated processing. With the transition of LANL analytical chemistry operations from a nuclear facility to a low-hazard radiological facility, there is a need to re-engineer the analytical chemistry flowsheet to reduce the overall quantity of plutonium that is processed during analysis of elemental and isotopic composition of metal and oxide samples. Additional benefits of microchemical separations include reduced waste generation and worker exposure.

Fabrication and testing of microfluidic chips for solvent extraction and ion exchange applications, and procurement and system testing of commercial millifluidic systems, will be discussed in the context of both of these application areas.

LA-UR-16-22763

Small-Scale Tests in Support of Chemical Processes for Production of Pu-238

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Abstract. Oak Ridge National Laboratory (ORNL) is currently working to reestablish the capability to produce plutonium dioxide ($^{238}\text{PuO}_2$) for use in radioisotope thermoelectric generators (RTGs) for deep space applications. Neptunium-237 targets are fabricated at ORNL's Radiochemical Engineering Development Center (REDC) and are currently being irradiated at the High Flux Isotope Reactor (HFIR), with plans to use Idaho National Laboratory's Advanced Test Reactor for additional irradiation capacity. Developmental studies examine the processing of the irradiated targets being performed in equipment installed in the hot cells and glove boxes at REDC. Plutonium oxide will be shipped to Los Alamos National Laboratory, while neptunium will be recovered and recycled for use in target fabrication at ORNL.

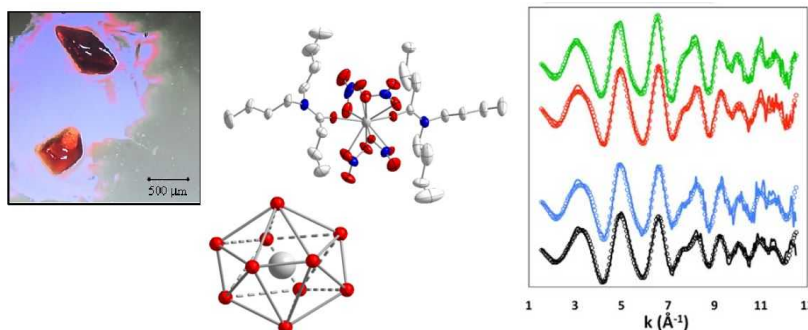
This presentation will provide an overview of the current status of chemical process testing but will focus on the small-scale tests carried out in glove boxes to provide information and improve the processes in the hot cells. The primary separation of the neptunium, plutonium, and fission products is accomplished by solvent extraction using countercurrent mixer-settler contactors. The plutonium product is purified and converted to PuO_2 by means of a newly developed version of a resin loading/calcination process. The neptunium is recovered and recycled by purification using ion exchange processes.

Keywords: Plutonium-238, production, chemical processing, solvent extraction, ion exchange

Structure and radiolytic stability of monoamide-actinide complexes

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CEA Marcoule



In the field of nuclear fuel reprocessing, N,N-dialkyl monoamides are alternative organic ligands to achieve the separation of uranium(VI) and plutonium(IV) from highly concentrated nitric acid solution. One of the very interesting features of these ligands is the strong influence of their alkyl groups on their extraction properties. It gives the possibility to tune their extracting strength and selectivity toward uranium (VI) and plutonium (IV) by altering the length and branching of monoamide alkyl chains. Despite their strong industrial interest, few basic studies have been reported on this effect and the understanding of this strong influence on monoamides extracting properties is yet to be achieved. Among the properties that are important for a comprehensive understanding of selective extraction processes, the stoichiometries and coordination structures of the actinide complexes in the organic solution can provide crucial information regarding extraction mechanisms. The study presented here combines experiments (EXAFS, XRD, ESI-MS) and theoretical calculations (DFT) aiming to describe the structures of the complexes formed between Pu(IV) and different N,N-dialkyl monoamides, and the impact of radiolysis on these complexes.

It is shown that the coordination structure of U(VI) is analogous in the solution and in the solid state and is independent of the alkyl chain: two monoamide ligands and four bidentate nitrate ions coordinate the uranyl ion. With linear alkyl chains monoamides, Pu(IV) also adopt identical structures in the solid state and in solution with two monoamides and four bidentate nitrate ions. With branched alkyl chain monoamides, the coordination structure of Pu(IV) was more difficult to establish unambiguously in solution. However, using a combination of EXAFS spectroscopy experiments with DFT calculations, it was possible to show that the branched alkyl chains amide form partly outer-sphere complexes with protonated ligands hydrogen bonded to nitrate ions, that could explain the different extraction properties of these ligands.

In the actinide solvent extraction processes, the organic solutions are subjected to radiolysis that can lead to an alteration of the ligands properties, and especially to their extraction efficiency and selectivity. Therefore, the effects of radiolysis on the speciation of the complexes in solution have been studied using ESI-MS spectrometry. Both gamma source irradiated solutions and direct in-situ alpha irradiated solutions have been studied in order to compare the nature of irradiation.

Calcium Reduction of Spent Electrorefining Salt

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Spent Electrorefining (ER) salt from the pyrochemical processing of plutonium at AWE is currently stored on site awaiting a suitable recovery route. Restrictions on the materials storage and disposal mean reprocessing is required to find a more suitable storage form and recover the plutonium metal. A Calcium Reduction process is currently being developed at AWE to treat spent ER salt residues.

The process aims to reduce the Pu^{3+} species in the spent salts to plutonium metal via the addition of calcium metal. The product is a consolidated plutonium button and salt residues that contain considerably lower levels of plutonium than before processing. In total, seven experiments have been carried out at AWE to demonstrate calcium reduction as a potential plutonium recovery process. Of the six experiments carried out; three experiments were on spent ER salt with no ceramic fines and four on spent ER salt containing ceramic fines. Alongside the experiments carried out on the two different salt feeds, varying levels of calcium were used in different runs to identify a suitable excess amount of calcium for the process.

Initial findings from AWE experiments show a high removal of plutonium in both types of spent ER salt, with or without ceramic fines. The product metal in most cases has formed a consolidated button which sometimes contains un-reacted calcium metal. The salt after assay and initial analysis has shown to contain very low levels of plutonium.



Figure 2: Photograph of the spent ER salt containing ceramic fragments after the calcium reduction process. This experiment used 30 % excess calcium. Two phases can be seen in the salt block. The white upper layer contains almost no plutonium. The darker layer is plutonium rich where partial reduction of the plutonium occurred. The bottom surface is the consolidated metal button.

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Historical Test Debris Analysis using Long Lived Lanthanides

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Los Alamos National Laboratory

To characterize a nuclear event it is essential to have methodologies for conducting a variety of technical nuclear forensics investigations. Among the many methods currently used, information associated with long-lived fission products are often excluded or ignored. Our goal is to develop analysis of long-lived fission products, specifically ^{147}Pm (100% β , $t_{1/2} = 2.62\text{y}$), ^{151}Sm (100% β , $t_{1/2} = 90\text{y}$) and ^{155}Eu (100% β , $t_{1/2} = 4.76\text{y}$), to obtain new data from old debris and make US Government forensic efforts more robust. Our approach will allow to re-evaluate old events with new measurements after the short-lived fission products already decayed. Lanthanides in general track plutonium in the environment and therefore they can be used to interrogate fission events that happened long time ago.

The analysis of long-lived lanthanides in environmental debris involves sample dissolution, series of precipitations to remove various contaminants which is followed by ion-exchange high performance liquid chromatography (HPLC) to separate individual neighboring lanthanides and concludes with quantification of individual lanthanide isotopes. In this contribution, novel approach to ^{151}Sm , ^{155}Eu quantification will be introduced. Previously isotopes of Eu and Sm were quantified gravimetrically by addition of known amount of stable elements to the sample. This method requires rather difficult separation of mg amounts of neighboring lanthanides. Our new approach to obtain recovery of the chemical procedure uses small amounts of enriched stable Eu and Sm isotopes and only several mg of lanthanum as a carrier for series of precipitation during chemical procedure. The novel approach allows to scale-down ion-exchange HPLC separation, resulting in 40% time and > 60% reagents reduction.

Quantification of small amounts of ^{147}Pm , ^{151}Sm and ^{155}Eu is rather difficult due to low energy beta decay. In this contribution we will introduce new method to quantification of ^{147}Pm and ^{151}Sm using microcalorimetric detectors.

LA-UR-16-21929

Alternative Chemical Cleaning Methods for High Level Waste Tanks

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Savannah River National Laboratory

Two series of solubility tests were performed to evaluate alternate chemical cleaning technologies for the dissolution of high level waste solids remaining in tanks after the exhaustion of mechanical cleaning and sludge washing efforts. Surrogate experiments were conducted with nonradioactive single phase reagents, binary mixtures of reagents, and an SRS PUREX tank waste heel to evaluate the effectiveness of dilute oxalic/nitric acid and dilute nitric acid cleaning processes in dissolving the bulk non-radioactive waste components. A focus of this testing was on minimization of oxalic acid additions during tank cleaning. In a separate study, solubility tests were conducted with a simulated radioactive waste tank heel using acidic and caustic permanganate-based methods. The focus of this study was the targeted dissolution of transuranic species known to be problematic in the SRS tank closure performance assessments. The permanganate-based cleaning methods were evaluated prior to and after contacting the simulated waste tank heel with oxalic acid using current waste tank cleaning practices.

Based on the results from the nonradioactive tests, significantly more oxalic acid than necessary has likely been used in previous tank chemical cleaning campaigns. Furthermore, oxalic acid was not effective in removing all sludge components (e.g., Ni and Hg). The baseline method was somewhat effective at removing most simulated sludge Mn components and very effective at removing Fe and Al (gibbsite). Dilute nitric/oxalic acid mixtures were effective in removing most primary (Fe and Al) and secondary (Mn, Ni and Hg) sludge phases. Dilute, nitric acid was effective in removing Al, Ni, Mn^{2+} , and Hg. A processing sequence involving dilute nitric acid followed by a dilute nitric/oxalic acid mixture appears to be the optimal cleaning approach resulting in minimal oxalate additions. This cleaning method requires larger water addition volumes than the baseline method; although, decreased subsequent water additions are expected during sludge washing since minimal sodium oxalate salts should be present in the sludge heel.

Solubility tests with a radioactive simulant prior to oxalic acid addition indicated that small amounts of transuranic elements can be solubilized (approximately 30% Pu, 10% Np, and 5% Am) using the caustic permanganate method. However, the measured actinide concentrations using the caustic permanganate method exceeded concentrations typically observed in waste supernate by several orders of magnitude, so there is potential for solubilizing significant amounts of actinides from residual solids using this method. When the radioactive sludge heel simulant was contacted with acidic permanganate solution, ~90% of the Np and Pu components were solubilized, indicating that solubility limits were probably not reached in these tests due to depletion of these species from the residual solids. In contrast, only ~50% of the Am was solubilized, which indicated that some interaction with a component in the simulated sludge or MnO_2 precipitate resulted in decreased Am solubility. Based on the results, it appears that the treatment of waste tank sludge residuals with an acidic permanganate solution has the potential to solubilize a higher fraction of the actinides than a caustic permanganate solution, although both methods were effective.

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